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# DETERMINATION OF THE CRYSTALLIZATION COEFFICIENTS FOR THE DISTRIBUTION OF RADIUM BETWEEN SALT MELTS AND CRYSTALS OF BARIUM OR LEAD CHLORIDE

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One of us, with Khlopin, has previously investigated the distribution of radium between a salt melt and crystals of a salt isomorphous with the corresponding radium salt [1].

It was found that, when a solid phase separates from the melt, the distribution of the microcomponent between the liquid and the solid phases proceeds, as it does in solutions, in accordance with Khlopin's law. In the systems examined - in which the solid phases were crystals of calcium, strontium, barium, and lead nitrates, and lead sulfate - the crystallization coefficient D (a measure of the enrichment of the separating crystals in the microcomponent, as compared with the salt remaining in the solution) was found to be constant, irrespective of the amount of solid phase that separated.

The values of the crystallization coefficients for the distribution of radium between salt melts and crystals in these systems are given in Table 1.

TABLE 1

| System | D |
|---|---|
| $Ca(NO_3)_2-Ra(NO_3)_2-NaNO_3$ | 1.00 |
| $Sr(NO_3)_2-Ra(NO_3)_2-KNO_3$ | 0.43 |
| $Ba(NO_3)_2-Ra(NO_3)_2-NaNO_3$ | 0.46 |
| $Pb(NO_3)_2-Ra(NO_3)_2-NaNO_3$ | 1.00 |
| $PbSO_4-RaSO_4-Li_2SO_4$ | 1.08 |

It will be seen from Table 1 that in all of the systems that have been studied the crystallization coefficient D is either less than or equal to unity. This indicates that either enrichment in radium occurs in the liquid phase, or the radium is evenly distributed between the two phases. This is the reverse from what has generally been observed when crystallization occurs from a solution: for most salts the crystals are enriched in the microcomponent, even at a temperature of about 100° [2].

It was of interest to determine whether the distribution of the microcomponent in this way during the separation of the solid phase from a melt is the normal behavior or is merely characteristic of these particular salts. We therefore decided to continue this line of investigation and to determine the crystallization coefficients for the distribution of radium between salt melts and crystals of barium or lead chloride.

We selected barium chloride as a macrocomponent because in its crystallization from solution, even at about 100°, the crystals that separate are about twice as rich in radium as the salt remaining in solution (D = 2.11 at 104.3°). Also, for barium chloride a suitable binary system can be found, i.e. one in which the components form no chemical compounds or solid solutions and in which the eutectic occurs at a relatively low temperature. As regards lead chloride, it is known that the radioactive lead isotopes (ThB and RaD) are coprecipitated with barium chloride and with radium chloride crystals when these separate from solution [3], so that these salts are isomorphous.

However, the coprecipitation of radium with lead chloride during the crystallization of the latter from solution has not been observed, but it is known that at high temperatures barium and lead chlorides form a continuous series of mixed crystals [4]. It was therefore of interest to determine the behavior of radium during the crystallization of lead chloride from a melt, since it would be expected, by analogy with barium, that under these conditions radium would also be coprecipitated with lead chloride, it being assumed that the close similarity in the properties of radium and barium is retained at high temperatures.

## EXPERIMENTAL

The experimental procedure applied in the determination of the crystallization coefficients of radium has already been described in detail [1].

1. Determination of the Crystallization Coefficient for the Distribution of Radium between the Melt and Barium Chloride Crystals in the System $BaCl_2-LiCl$

The distribution of radium between melt and barium chloride crystals was studied in the binary system $BaCl_2-LiCl$, which has a eutectic at a relatively low temperature (510° according to Sandonnini) and gives melting point curves that correspond to the crystallization of the pure components.

The salts used in our experiments were first purified and dehydrated. Barium chloride was recrystallized and then dehydrated by drying it to constant weight at 120-125°. The lithium chloride contained a small amount of iron

impurity, and was therefore purified by treatment with ammonia, which precipitated ferric hydroxide. It was not possible to dehydrate lithium chloride by simple drying, since hydrolysis would occur.

According to the literature [5] anhydrous lithium chloride can be prepared either by the evaporation of a solution of lithium chloride to dryness in a current of hydrogen chloride, or by addition of ammonium chloride to an evaporating solution of the salt and heating of the dry residue, when the ammonium chloride is decomposed into ammonia and hydrogen chloride. We used the second method. The lithium chloride solution was filtered from the ferric hydroxide, and an equivalent amount of ammonium chloride was added. The solution was evaporated to dryness in an air bath, and the residue was then heated in a loosely covered platinum dish to remove ammonium chloride. At first the residue was heated cautiously in order to remove residual water, it was then heated more strongly (decomposition of ammonium chloride into ammonia and ammonium chloride occurs at 335°). After removal of ammonium chloride the salt formed a white spongy mass, which was readily loosened from the walls of the dish.

As a check on the purity of the lithium chloride its melting point was determined and found to be 608°. The values given in the literature by various authors range from 602° to 614° [6]. The anhydrous salt was kept in a carefully sealed jar in a desiccator. All operations with lithium chloride were performed as quickly as possible, and the weights of samples were determined by the difference method.

The fusion of mixtures of barium chloride and lithium chloride for the determination of the melting curve of the system and for the distribution experiments was carried out in a porcelain crucible in an electric crucible furnace. The temperature of the melt was determined with the aid of a thermocouple of platinum and platinum-rhodium, which was graduated without a sheath at the freezing points of various salts.

On our fusion diagram of the binary system $BaCl_2$—LiCl the melting point of the eutectic is 510°, and the eutectic composition is 37.5 mole % $BaCl_2$ and 62.5 mole % LiCl. Our results are in good agreement with those of Sandonnini [7], who gives the eutectic melting point as 510° and the composition as 35 mole % $BaCl_2$ and 65 mole % LiCl. The determination of the radium contents of test samples of the melt taken before and after the separation of the solid phase was carried out by the emanation method.

In the determination of the crystallization coefficient for the distribution of radium between the melt and barium chloride crystals, nine experiments were carried out. Solid phase was allowed to separate from the saturated melt over the temperature range 711–522°. The results are given in Table 2.

TABLE 2

Distribution of Radium between the Melt and $BaCl_2$ Crystals in the Binary System $BaCl_2$—LiCl

| Expt. No. | Amount of $BaCl_2$ separated as solid phase (%) | Amount of Ra separated in solid phase (%) | D |
|---|---|---|---|
| 1 | 8.7 | 7.9 | 1.03 |
| 2 | 15.6 | 15.0 | 1.02 |
| 3 | 23.5 | 25.6 | 1.04 |
| 4 | 31.5 | 29.6 | 0.81 |
| 5 | 32.5 | 39.6 | 1.14 |
| 6 | 37.7 | 35.5 | 0.91 |
| 7 | 39.6 | 41.4 | 1.08 |
| 8 | 46.4 | 48.4 | 1.06 |
| 9 | 50.8 | 52.6 | 1.05 |

It will be seen from Table 2 that, although there is a sevenfold variation in the amount of solid phase separated, the crystallization coefficient D remains constant at 1.03. These results indicate that in this system, as in all of the previous systems that we have studied, no enrichment of the solid phase in radium occurs when radium becomes distributed between the melt and the crystals of a salt that is isomorphous with the corresponding radium salt.

## 2. Determination of the Crystallization Coefficient for the Distribution of Radium between the Melt and Lead Chloride Crystals in the System $PbCl_2$—NaCl

We have determined the crystallization coefficient for the distribution of radium between the melt and lead chloride crystals in the binary system $PbCl_2$—NaCl, which, according to the literature [8], has a eutectic point, melting point 411°, and composition 27 mole % NaCl, 73 mole % $PbCl_2$.

Under the action of light and when heated in air lead chloride decomposes with formation of the oxychloride. The latter, however, can even be sublimed without decomposition in an inert atmosphere. Recrystallized lead chloride was therefore dried, first by exposure to the atmosphere in the dark, and then, again in the dark, over phosphoric oxide in a vacuum desiccator. Also, immediately before the experiment, the lead chloride and sodium chloride were fused for some time in a crucible furnace at about 550°, the lead chloride being treated in an atmosphere of carbon dioxide.

The experiments for the determination of the melting diagram of the system and for the determination of

the radium crystallization coefficient were also carried out in an inert atmosphere. Melts produced under these conditions were transparent and of a light yellow color, which indicated absence of decomposition.

In this work we again used procelain crucibles, since it is not advisable to keep molten lead chloride in contact with platinum for a long time. Although lead chloride sublimes when heated, it was found by a special experiment that the losses from this source comprised a negligible part of the lead chloride taken for the determinations.

Our melting curve for the system $PbCl_2$–NaCl has a eutectic having a melting point of 409° and a composition of 70.7 mole % $PbCl_2$ and 29.3 mole % NaCl. The results of the experiments on the determination of the crystallization coefficient for the distribution of radium between the melt and lead chloride crystals are given in Table 3.

TABLE 3

Distribution of Radium between the Melt and $PbCl_2$ Crystals in the Binary System $PbCl_2$–NaCl

| Expt. No. | Amount of $PbCl_2$ separated as solid phase | Amount of Ra separated in the solid phase (%) | D |
|---|---|---|---|
| 1 | 30.0 | 26.2 | 0.83 |
| 2 | 42.5 | 40.4 | 0.91 |
| 3 | 44.6 | 43.3 | 0.95 |
| 4 | 51.5 | 48.4 | 0.88 |
| 5 | 52.3 | 50.3 | 0.92 |
| 6 | 61.7 | 59.4 | 0.90 |
| 7 | 62.4 | 57.7 | 0.82 |
| 8 | 63.0 | 59.5 | 0.86 |
| 9 | 65.7 | 61.3 | 0.82 |
| 10 | 69.0 | 65.8 | 0.87 |
| 11 | 78.2 | 74.0 | 0.79 |

Mean 0.85 ± 0.04

TABLE 4

Values of the Crystallization Coefficient of Radium for various Concentrations of Radium in the Original Melt

| Expt. No. | Ra Concentration in the original melt (g of Ra per gram of melt) | D |
|---|---|---|
| 1 | $2.0 \cdot 10^{-9}$ | 0.81 |
| 2 | $8.3 \cdot 10^{-8}$ | 0.91 |
| 3 | $1.1 \cdot 10^{-7}$ | 0.85 |
| 4 | $2.1 \cdot 10^{-5}$* | 0.91 |
| 5 | $1.9 \cdot 10^{-2}$ | 0.93 |

Mean 0.88 ± 0.04

* Increase in the concentration of the microcomponent was produced as a result of the addition of the corresponding amount of barium

In this series of experiments the solid phase was allowed to separate from the saturated melt over the temperature range 490–440°. Altogether, eleven determinations were made of the crystallization coefficient for the distribution of radium between the melt and $PbCl_2$ crystals. The crystallization coefficient D remained constant while the amount of separated solid phase varied by a factor of 2.5; its numerical value was 0.85.

Unlike the crystallization coefficient for the distribution of radium between a salt melt and lead nitrate or sulfate crystals (which has the value of unity), the crystallization coefficient in the present system is less than unity, so that again there is no enrichment of the solid phase in radium.

We carried out a second series of experiments for this system. In these we determined the crystallization coefficients of radium for various concentrations of radium in the original melt. As will be seen from Table 4, a change by a factor of several powers of ten in the radium concentration in the original melt has no effect on the value of the crystallization coefficient D.

In 1950 Khlopin formulated the following rule [9]: "If the distribution of a microcomponent (radioelement) between a solid crystalline phase and a solution is strictly in accord with the law for the distribution of a substance between two immiscible solvents and the crystallization coefficient D remains constant while the concentration of the substance being distributed varies over a wide range (by a factor of several powers of ten), then it may be considered to be proved that the Mitscherlich law can be extended to the given pair of substances, i.e. that the macro- and microcomponents are similar in chemical composition and molecular structure".

The constancy of the values of the crystallization coefficients that we have obtained for various concentrations of radium in the original solution in experiments on the distribution of radium between the melt and $PbCl_2$ crystals indicates, according to Khlopin's rule, that radium chloride crystallizes from the melt as the anhydrous chloride, isomorphous to lead chloride, i.e. behaves under these conditions as barium chloride does.

## SUMMARY

1. The crystallization coefficients have been determined for the distribution of radium between a salt melt and

and barium chloride crystals and between a salt melt and lead chloride crystals.

2. It has been shown that in these two systems, as in previously studied systems in which radium is distributed between the melt and salts isomorphous with the corresponding radium salts, no enrichment of the solid phase in radium occurs.

3. It has been shown that the closeness in chemical properties of radium and barium is preserved at high temperatures.

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# KINETICS OF THE OXIDATION OF SIMPLE UNSATURATED HYDROCARBONS IN THE PRESENCE OF VANADIUM CONTACT CATALYSTS

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In the previous investigations [1] the use of labeled carbon ($C^{14}$) has enabled us to establish the main directions of reaction in the oxidation of ethylene and propene in presence of vanadium catalysts. The isotopic composition of the products showed that the process by which part of the carbon monoxide and dioxide was formed from the hydrocarbon was independent of that leading to the formation of acetaldehyde and ethylene oxide, and that these last substances could not be the main intermediate products in the destructive oxidation of the hydrocarbons. A comparative study by Andrianova and Roginsky [2] of the oxidation of propene and oxygen-containing substances (aldehydes and acids) over vanadium catalysts has shown that the low yields of aldehydes can be explained by their instability under the conditions of the experiment.

## EXPERIMENTAL

The kinetics of the oxidation of ethylene and propene in mixtures of these hydrocarbons with air was studied under dynamic conditions at atmospheric pressure. We have determined the conditions required for the maintenance of isothermal conditions in investigations on the destructive oxidation of hydrocarbons [3]. The reaction products were analyzed as follows:

a) Organic acids were determined by titration to phenolphthalein with 0.01 N KOH.

b) Aldehydes were determined by the hydroxylamine method. In some cases determinations were made also of the proportions of acetaluehyde and formaldehyde by a polarographic method.

c) Gaseous products were analyzed for their contents of $CO_2$, CO, $O_2$, $H_2$, and hydrocarbons in the VTI gas analysis apparatus.

The kinetics of the oxidation of the hydrocarbons and certain of their reaction products (acetaldehyde and carbon monoxide) were studied also under static conditions at pressures of the order of 0.5 mm Hg. In these experiments aldehyde was separated by freezing it out in a trap immersed in a cryostat containing solid propyl alcohol (−126°), and carbon dioxide was absorbed with solid caustic potash. Carbon monoxide was mixed with oxygen and the mixture was ignited with an incandescent platinum wire, the resulting carbon dioxide was frozen out in a trap at the temperature of liquid nitrogen.

### Catalyst

Ammonium vanadate was applied from solution to active silica having a specific surface of 300 sq. m per gram. The product was dried and the ammonium vanadate was converted into $V_2O_5$ at 400°. Activation in a current of a nitrogen–hydrocarbon mixture yielded a catalyst which was found by X-ray analysis to contain a mixture of vanadium pentoxide and tetroxide. In the experiments carried out in the static apparatus, separate studies were made of the catalytic effects of pure vanadium pentoxide and pure vanadium tetroxide without carriers.

The experiments in the dynamic apparatus were carried out for 30 minutes at the selected temperature and a fresh sample of catalyst was taken for each experiment. This procedure ensured good reproducibility of results. Before oxidation under static conditions, the catalyst was activated at 450°. Sorption of oxygen was then carried out at the same temperature and at a pressure of 2 mm Hg, after which the temperature was lowered and the excess of oxygen was pumped off.

### Kinetics of the Oxidation of Propene over Vanadium Catalysts

The products of the oxidation of propene with oxygen or air in presence of vanadium catalysts include aldehydes, acids, carbon monoxide and dioxide, hydrogen, methane, and water. According to Tikhomirova's results [4], in the oxidation of ethylene the carbon monoxide content of the gas is twice as high as the carbon dioxide content. The only aldehyde present is formaldehyde, without acetaldehyde impurity. Pigulevsky and Yarchemskaya [5] showed that in the oxidation of propene the formation of 1 liter of gaseous aldehydes was accompanied by the formation of 0.1 liter of acids, 1 liter of carbon dioxide, and 1.8 liter of carbon monoxide, i.e. the ratio of CO to $CO_2$ was again close to two. There was more acetaldehyde than formaldehyde in the reaction products, and no propylene oxide could be detected.

was more acetaldehyde than formaldehyde in the reaction products, and no propylene oxide could be detected.

The composition of the oxidation products of hydrocarbons depends greatly on the concentrations of the starting materials. Isotope tracer experiments show that the process proceeds in several directions simultaneously. Each of these transformations is made up of a number of stages in which ordinary stable molecules and also labile forms (radicals, atoms, and ions) can take part. Confining the analysis of products to stable molecules, we may distinguish primary and secondary products for each direction of reaction.

The following processes have been detected with the aid of molecules labeled with $C^{14}$:

1. Formation of aldehydes with the possibility a) of sub. c.. ent decomposition with generation of carbon monoxide, b) oxidation to carbon dioxide, and c) oxidation to carboxylic acids (which are probably formed also without intermediate formation of aldehydes).

2. Oxidation of olefin oxides, followed by isomerization, decomposition, and oxidation of these.

3. Oxidation to carbon monoxide and dioxide without intermediate formation of aldehydes and olefin oxides, the probable intermediate being of the peroxide type. The oxidation of hydrocarbons via olefin oxides has been studied to a less extent owing to the high reactivities of the latter, and we shall confine ourselves to the analysis of the kinetics of reactions characterizing the first and third processes.

In order to determine order and rate constants for each of the component reactions: a) the contents of propene and oxygen in the reaction mixture were each varied from 4 to 27%, while maintaining the ratio of the concentrations constant; b) the content of oxygen was varied (2-14%) at a constant hydrocarbon concentration (4%).

Tables 1, 2, and 3 give the rate constants, calculated for zero- and first-order reactions, for the formation of aldehydes, carbon dioxide, and carbon monoxide respectively from propene.

For these three reactions the rate constants calculated from the zero-order equation increase as the concentrations of propene and oxygen increase. The reaction must therefore be of a higher order. When the concentrations of propene and oxygen are increased by a factor of 6-7, the rate constants calculated from the first-order equation remain practically constant, which indicates the applicability of this equation. Our calculations from the data of Bretter, Shen-Wu-Wen, and Dodge [6] (Table 4) on the oxidation of isobutene over $V_2O_5$ are in accord with our data on the oxidation of propene. Table 5 gives the rate constants with respect to oxygen for these reactions.

TABLE 1

Rate Constants for the Oxidation of Propene to Aldehydes

| No. | Initial concentration of $C_3H_6$, $c_p$ | Initial concentration of oxygen, $c_o$ | Zero-order constant, $k_0$ | First-order constant, $k_1$ | Notes |
|---|---|---|---|---|---|
| 1 | 2 | 2.4 | 0.3 | 0.070 | The oxidation experiments were carried out with simultaneous variation in the concentrations of the two reactants, and the reaction order has an overall value for ($O_2$ - $C_3H_6$) |
| 2 | 4 | 4.0 | 0.5 | 0.068 | |
| 3 | 6 | 6.0 | 0.6 | 0.067 | |
| 4 | 8 | 8.0 | 1.28 | 0.065 | |
| 5 | 10 | 10.4 | 1.80 | 0.070 | |
| 6 | 12 | 12.5 | 2.2 | 0.070 | |
| | | Mean | | 0.068 | |

A sevenfold increase in the concentration of oxygen in the reaction mixture at a constant concentration of propene did not affect the rate constants for the reaction calculated from the first-order equation.

A comparison of Tables 1-3 shows that the first-order kinetics are determined by the oxygen, there being almost no effect ascribable to the concentration of hydrocarbon. The kinetic equations for the formation of aldehydes, carbon dioxide, and carbon monoxide from propene can therefore be written as follows:

$$1.\ \frac{d[ald]}{dt} = k_1[C_3H_6]^0[O_2]^1,$$

$$2.\ \frac{d[CO_2]}{dt} = k_1'[C_3H_6]^0[O_2]^1,$$

$$3.\ \frac{d[CO]}{dt} = k_1''[C_3H_6]^0[O_2]^1.$$

Fig. 1 shows the dependence of the logarithm of the rate constants for the formation of aldehydes, $CO_2$, and

CO from propene on 1/T. It will be seen that the relation between the rate constants and temperature is in accord with the Arrhenius law. The activation energies E are given in Table 6. Apart from our own results, Table 6 and Fig. 1 include data calculated from the results of Tikhomirova on the oxidation of ethylene and Brenton, Shen-Wu-Wan, and Dodge on the oxidation of isobutene. It is noteworthy in Table 6 that the activation energies for the formation of carbon dioxide are high and are equal for ethylene and propene. On the other hand, the activation energies for the formation of aldehydes from propene and isobutene are very low, but are again almost equal.

TABLE 2

Rate Constants for the Oxidation of Propene to $CO_2$

| No. | Initial concentration of $C_3H_6$, $c_0$ | Initial concentration of oxygen, $c_0'$ | Zero-order constant, $k_0$ | First-order constant, $k_1$ | Notes |
|---|---|---|---|---|---|
| 1 | 2 | 2.4 | 0.28 | 0.040 | Order of reaction has an overall value for $(C_3H_6 + O_2)$ |
| 2 | 4 | 4.0 | 0.45 | 0.054 | |
| 3 | 6 | 6.0 | 0.70 | 0.054 | |
| 4 | 8 | 8.0 | 0.90 | 0.054 | |
| 5 | 10 | 10.0 | 1.1 | 0.054 | |
| 6 | 12 | 12.0 | 1.25 | 0.054 | |
| | | | Mean | 0.0515 | |

TABLE 3

Rate Constants for the Oxidation of Propene to CO

| No. | Initial concentration of $C_3H_6$, $c_0$ | Initial concentration of oxygen, $c_0'$ | Zero-order constant, $k_0$ | First-order constant, $k_1$ | Notes |
|---|---|---|---|---|---|
| 1 | 2 | 2.4 | 0.12 | 0.036 | Order of reaction has an overall value for $(C_3H_6 + O_2)$ |
| 2 | 4 | 4.0 | 0.22 | 0.036 | |
| 3 | 6 | 6.0 | 0.52 | 0.038 | |
| 4 | 8 | 8.0 | 0.76 | 0.040 | |
| 5 | 10 | 10.0 | 0.96 | 0.040 | |
| 6 | 12 | 12.0 | 1.19 | 0.040 | |
| 7 | 14 | 14.0 | 1.20 | 0.038 | |
| | | | Mean | 0.038 | |

TABLE 4

Rate Constants for the Oxidation of Isobutene to CO and $CO_2$ over $V_2O_5$ (calculated from data of Brenton, Shen-Wu-Wan, and Dodge) at 400°

| No. | Initial concentration of isobutene, $c_0$ | Time of contact (sec) | First-order rate constant for formation of CO | First-order rate constant for formation of $CO_2$ | Notes |
|---|---|---|---|---|---|
| 1 | 0.76 | 0.1 | 0.43 | 0.25 | Order of reaction has an overall value for $(C_4H_8 + O_2)$ |
| 2 | – | 0.2 | 0.049 | 0.025 | |
| 3 | – | 0.3 | 0.049 | 0.029 | |
| 4 | – | 0.4 | 0.049 | 0.028 | |
| 5 | – | 0.5 | 0.049 | 0.025 | |
| 6 | – | 0.6 | 0.048 | 0.025 | |
| 7 | – | 0.8 | 0.047 | 0.023 | |
| 8 | – | 0.9 | 0.047 | 0.025 | |
| 9 | – | 1.1 | 0.048 | 0.025 | |
| | | Mean | 0.048 | 0.025 | |

The low activation energies for the formation of aldehydes and carbon monoxide do not appear to be explicable on the assumption that these reactions occur in the diffusion or intermediate zone, since the absolute values of the rates of the reactions are lower than the rate of formation of carbon dioxide.

TABLE 5

Rate Constants with Respect to Oxygen for the Formation of Aldehydes, $CO_2$, and CO

| No. of the concentration region | Initial concentration of propene $c_p$ | Initial concentration of oxygen $c_0$ | First-order rate constants: for the formation of aldehydes | for the formation of $CO_2$ | for the formation of CO |
|---|---|---|---|---|---|
| 1 | 4.0 | 2 | 0.070 | 0.098 | 0.036 |
| – | – | 4 | 0.068 | 0.10 | 0.036 |
| 3 | – | 6 | 0.069 | 0.11 | 0.038 |
| 4 | – | 8 | – | 0.11 | 0.040 |
| 5 | – | 10 | – | 0.12 | 0.040 |
| 6 | – | 12 | – | 0.12 | 0.040 |
| 7 | – | 14 | – | 0.12 | 0.038 |
| | | Mean | 0.069 | 0.11 | 0.038 |

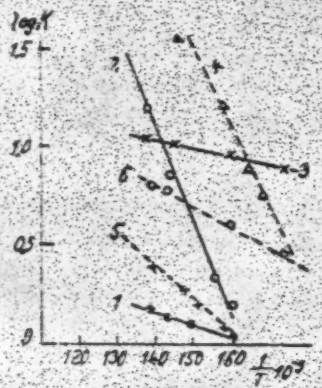


Fig. 2. Dependence of the logarithms of the rate constants for the formation of aldehydes, $CO_2$, and CO from various unsaturated hydrocarbons on 1/T: 1) aldehydes; 2) $CO_2$; 3) CO; 4) $CO_2$ from Tikhomirova's data; 5) CO from Bretton, Sher-Wu-Wan, and Dodge's data; 6) CO from Tikhomirova's data.

TABLE 6

Activation Energies E for the Formation of Aldehydes, Carbon Dioxide, and Carbon Monoxide from Various Hydrocarbons

| Reaction | Hydrocarbon | Activation energy (kcal/mole) | Author |
|---|---|---|---|
| Formation of aldehydes | Propene | 4 | the present authors |
| Formation of $CO_2$ | " | 22 | |
| Formation of CO | " | 2 | |
| Formation of $CO_2$ | Ethylene | 21 | Tikhomirova [2] |
| Formation of CO | " | 5 | |
| Formation of CO | Isobutene | 7 | Bretton, Sher-Wu-Wan, and Dodge [6] |
| Formation of formaldehyde | " | 5 | |

The main secondary reactions in the oxidation of hydrocarbons over vanadium catalysts are the decomposition and oxidation of aldehydes:

$$a)\ RCHO \longrightarrow CO + RH,$$

$$b)\ RCHO \xrightarrow{O_2} CO_2 + H_2O$$

$$c)\ 2CO + O_2 \longrightarrow 2CO_2$$

Over $V_2O_5$ at 300-400° carbon monoxide is oxidized to a comparatively small extent (10-15%). Over $V_2O_4$ extents of the conversion into $CO_2$ is much greater (50-60%). These reactions were studied under static conditions over pure vanadium oxides $V_2O_5$ and $V_2O_4$.

Tables 7 and 8 give the values of the rate constants for the decomposition and oxidation of acetaldehyde over $V_2O_5$ and $V_2O_4$.

The constancy of the values for the rate constants for the decomposition of aldehydes indicates the application of a first-order equation, except in the very beginning of the reaction. The oxidation of acetaldehyde to $CO_2$ proceeds by a reaction of fractional order (0.2), except in the early stages.

Fig. 3 gives characteristic curves for the consumption of acetaldehyde and the formation of $CO_2$ over $V_2O_5$. The rapid change in the acetaldehyde concentration at the beginning of the reaction probably results from its adsorption on the surface of the catalyst and probably explains the anomalous initial rate constants for the decomposition of aldehydes.

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The rate constants for the formation of aldehydes were calculated only as far as the maximum on the curve for the yield of aldehydes as a function of the oxygen concentration.

composition and oxidation of acetaldehyde. A study of the oxidation of acetaldehyde labeled with radiocarbon ove $V_2O_5$ has shown that the aldehyde is taken up rapidly and firmly by the catalyst surface [2]. The noncorrespondence of the rate of formation of $CO_2$ and the rate of consumption of acetaldehyde may be a result of the slowness of the oxidation of the aldehyde adsorbed on the catalyst to $CO_2$.

TABLE 7

Rate Constants for the Decomposition of Acetaldehyde over $V_2O_5$ and $V_2O_4$ at 350°

| Catalyst | Duration of reaction (min) | Initial concentration of $CH_3CHO$, $c_0$ | Initial concentration of oxygen, $c_0'$ | Zero-order rate constant, $k_0$ | First-order rate constant, $k_1$ | Notes |
|---|---|---|---|---|---|---|
| $V_2O_5$ | 10 | 0.65 | 0.35 | 0.39 | 0.057 | The value of $k_1$ for the first point is out of line with the others |
| | 15 | | | 0.45 | 0.036 | |
| | 20 | | | – | 0.038 | |
| | 25 | | | 0.48 | 0.032 | |
| | 30 | | | 0.51 | 0.033 | |
| | 35 | | | 0.54 | 0.035 | |
| | 40 | | | 0.57 | 0.035 | |
| | | | Mean (without first point) | | 0.034 | |
| $V_2O_4$ | 10 | 0.64 | 0.34 | – | 0.041 | The value of $k_1$ for the first point is out of line with the others |
| | 15 | | | – | 0.030 | |
| | 20 | | | – | 0.025 | |
| | 25 | | | – | 0.024 | |
| | 30 | | | – | 0.025 | |
| | 35 | | | – | 0.024 | |
| | 40 | | | – | 0.025 | |
| | | | Mean (without first point) | | 0.025 | |

TABLE 8

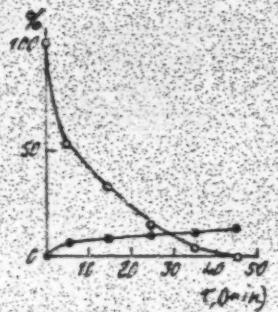
Rate Constants for the Oxidation of Acetaldehyde over $V_2O_5$

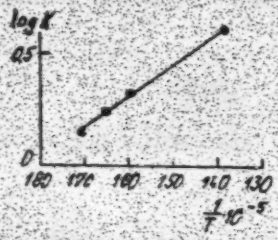
| Duration of reaction (min) | Initial concentration of $CH_3CHO$, $c_0$ | Initial concentration of oxygen, $c_0'$ | Zero-order rate constant, $k_0$ | First-order rate constant, $k_1$ | Fractional-order rate constant, $k_f$ |
|---|---|---|---|---|---|
| 10 | 0.65 | 0.35 | 0.14 | 0.069 | 0.060 |
| 15 | | | 0.17 | 0.054 | 0.055 |
| 20 | | | 0.19 | 0.047 | 0.050 |
| 25 | | | 0.22 | 0.043 | 0.045 |
| 30 | | | 0.24 | 0.040 | 0.045 |
| 35 | | | 0.26 | 0.037 | 0.040 |
| 40 | | | 0.28 | 0.035 | 0.040 |
| | | | Mean (without first and second points) | | 0.048 |

Hence the kinetic orders and the activation energies have been found for primary and secondary reactions (Table 9) in the oxidation of propene over vanadium catalysts.

The closeness of the values of the activation energies for the formation and decomposition of aldehydes makes it impossible to regulate their accumulation among the reaction products by variations in temperature. The small differences found in the values of the activation energies for the formation of aldehydes, carbon monoxide, and carbon dioxide as we pass from one unsaturated hydrocarbon to another (ethylene, propene, isobutene) make it probable that the primary act of the oxidation is essentially the same in each case, leading finally to the cleavage of the molecule of the unsaturated hydrocarbon at the double bond. The difference in activation energy for the formation of carbon monoxide and the formation of carbon dioxide points to the independence of these two processes. Although the activation energies are so greatly different for these reactions, the reaction rates are similar. This makes it probable that there are great qualitative differences between the processes; thus the formation of $CO_2$ may be a heterogeneous

homogeneous reaction, whereas the formation of CO may be purely heterogeneous. Experiments on the oxidation of propene with heavy oxygen lend support to this suggestion [7]. The oxygen of the catalyst takes a leading part in the formation of carbon monoxide, but does not take such an important part in the formation of carbon dioxide. Also different sites on the active surface may participate in these two independent reactions. Carbon monoxide, for example, may be formed on almost all of the sites on the catalyst surface, whereas the formation of $CO_2$ may occur on only a small fraction of them.



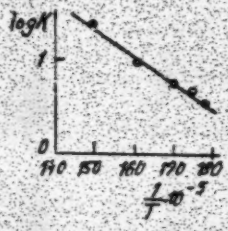




Fig. 3. Dependence of the logarithm of the rate constant for the decomposition of acetaldehyde over $V_2O_5$ on 1/T

Fig. 4. Dependence of the logarithm of the rate constant for the oxidation of CO to $CO_2$ over $V_2O_5$ on 1/T

TABLE

Activation Energies for the Primary and Secondary Oxidation Reactions of Simple Unsaturated Hydrocarbons

| No. | Reaction | Order of Reaction | Activation energy (kcal/mole) | Notes |
|---|---|---|---|---|
| 1 | Formation of aldehydes | First | 4-5 | Data on the oxidation of CO refer to $V_2O_5$ |
| 2 | Formation of carbon dioxide | " | 21-22 | |
| 3 | Formation of carbon monoxide | " | 2-7 | |
| 4 | Decomposition of aldehydes | " | " | |
| 5 | Oxidation of aldehydes | Fractional (0.2) | 5-8 | |
| 6 | Oxidation of carbon monoxide | First | 13 | |

The similarity of the kinetics of the component reactions, as established in this work, and their resemblance to the kinetics of the oxidation of ethylene to ethylene oxide in presence of silver make it necessary to examine critically the existing theories for the catalytic process and to make refinements in the proposed mechanisms for the oxidation of simple unsaturated hydrocarbons.

## SUMMARY

1. Acrolein, carbon monoxide, and carbon dioxide, produced by the oxidation of propene over vanadium catalysts, are formed by first-order reactions.

2. The first-order kinetics of these reactions are determined by the oxygen, their rates being almost independent of the hydrocarbon concentration under the conditions studied.

3. The activation energies have been determined for the formation of aldehydes, carbon monoxide, and carbon dioxide from simple unsaturated hydrocarbons. The activation energy for the formation of carbon dioxide is much higher than the activation energies for the formation of carbon monoxide and of aldehydes, which are themselves very close in value.

4. The kinetics of the decomposition and oxidation of acetaldehyde in presence of vanadium catalysts have been studied, and the activation energies of these reactions have been determined.

5. The relative values of the activation energies for the vanadium-catalyzed primary and secondary oxidation reactions of the unsaturated hydrocarbons studied are such that it is impossible to effect a substantial increase in the aldehyde content of the reaction products by changes in the temperature of the process and the concentrations of the reactants.

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# INVESTIGATION OF ELECTRODE PROCESSES OCCURRING DURING DEPOSITION AND DISSOLUTION OF SILVER IN CYANIDE SOLUTIONS

A. P. Popkov and A. T. Vagramyan

In the literature of electrochemistry there are many papers relating to investigations on electrode processes occurring during the deposition of metals in cyanide solutions [1]. A shortcoming of these papers lies in the fact that the explanations of the mechanism of the electrode processes and the character of the polarization are based solely on the basis of the forms and slopes of the curves for the dependence of polarization on current density. However, this relationship often does not give a complete picture of the processes occurring at the electrode under investigation, for it gives no idea at all of the changes in polarization with time. It is known that in the deposition and dissolution of metals polarization is not stable and changes with time [2], so that the forms and slopes of the polarization curves depend not only on the current density (other conditions remaining constant), but also on the rate at which the determination is made [3]. In a more detailed investigation of the electrode processes, therefore, it is necessary to study not only the dependence of polarization on current density, but also the change of polarization with time*. In the present investigation a study has been made of some processes occuring at a silver electrode polarized by alternating and intermittent currents.

## EXPERIMENTAL

### Experimental Procedure

The deposition and dissolution of silver was effected by alternating and intermittent currents obtained with the aid of a special commutator. A diagram of the commutator and the apparatus for recording changes in polarization is given in Fig. 1. The commutator consists essentially of an electromagnetic relay 1 and a switch-over disk 5. The electromagnetic relay effects the reversal of the polarizing current in the circuit II, and the frequency of the reversal and the time for which the current passes in the forward or reverse direction is regulated with the aid of the disk 5. The disk is made of insulating material and has a number of metallic contacts on its edge which can be connected to the metal ring C. When the disc is rotated at a definite given speed, one of the contacts (for example, ab), in passing under the brush C periodically makes and breaks the circuit feeding the electromagnetic coil 2 for a time proportional to the length of the metallic contact. When the circuit I is broken, the movable contacts 3 of the electromagnetic relay are pressed against the lower plates, as in Fig. 1, and the current flows in one direction. When the contact ab passes under the brush C, the circuit I is closed and the current, passing through the coil of the relay, switches the movable contacts 3 over on to the upper plates 4, and so changes the current in the electrolytic cell 13 over into the other direction. The durations of the positive and negative impulses can be varied over a wide range by increasing or diminishing the length of the contact ab and by changing the rate of rotation of the disk 5 with the aid of the gear box 7, which is connected to the electric motor 8. In order to obtain an intermittent current, i.e. a current that is interrupted periodically, the switch K is switched off, so that the current will pass in one direction for a time proportional to the length of the contact ab, and no current at all will pass for a time proportional to the insulated section bca.

Thus, with the aid of this commutator electrodes can be polarized both by alternating currents and by intermittent currents over a wide range of frequencies. As the processes investigated occupied such short periods of time, the polarization was recorded automatically with the aid of a cathode voltmeter 12 and a short-period (0.01 sec) mirror galvanometer 10. The record was produced with the light beam 11, which was reflected by the mirror of the galvanometer onto highly sensitive photographic film in the camera 9.

### Experimental Results

With the aid of the above-described method, a study was made of the variation of polarization with time for a given constant value of the current**. Fig. 2 shows the cathode polarization curves for a current density of 5 ma/sq.cm in the solution: $K[Ag(CN)_2]$ – 0.25N, KCN – 0.38 at 18-20°.

*This sort of investigation is particularly necessary in various cases of nonstationary electrolysis, for example, when polarization is effected by alternating current [4], or when alternating current is superimposed on direct, etc.

**Constancy of polarizing current was attained by the inclusion in the circuit of a large resistance 17, much greater than the internal resistance of the electrolytic cell.

These curves show that, after the current has been switched on, the cathodic polarization rises comparatively slowly: after 0.15 second it is 50 mv (Curve 3). When the duration of electrolysis is increased to 0.84 second, the cathodic polarization attains [illegible] mv (Curve 2); [illegible] 9.15 seconds it rises to 164 mv (Curve 1). The cathodic polarization comes to a stop after 2-3 minutes, and its absolute value attains 300 mv.

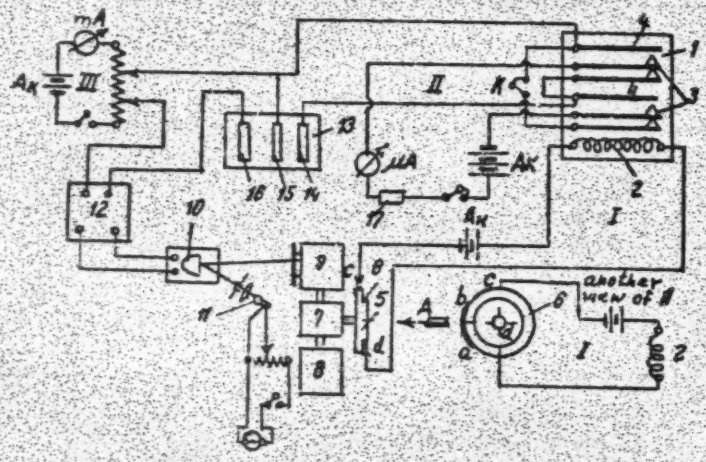


Fig. 1. Diagram of apparatus for the measurement of polarization during electrolysis with alternating and intermittent currents. 1) electromagnetic relay; 2) relay winding; 3) relay contacts; 4) upper plates; 5) Plexiglas disk; 6) metal ring; 7) gear box; 8) electric motor; 9) camera; 10) mirror galvanometer; 12) cathode voltmeter; 13) electrolytic cell; 15) investigated electrode; 16) auxiliary calomel electrode; 17) resistance

Fig. 3 shows curves for the change in anodic polarization with time, determined under the same conditions. When the current is applied to the electrode for 0.15 second, the anodic polarization attains 50 mv (Curve 3); when the duration of electrolysis is increased to 0.84 second, the polarization rises to 57 mv (Curve 2); and after 9.15 seconds it becomes 65 mv (Curve 1). Anodic polarization comes to a stop after 2-2.5 minutes, and its value attains [illegible]. When the curves in Figures 2 and 3 are compared it will be seen that the absolute values of the anodic polarization are lower than those of the cathodic polarization. This is evidence of the great difficulty of the cathode process in comparison with the anode process at the same current density (5 ma/sq.cm).

Fig. 4 shows the curve for the change in the cathodic and anodic polarizations with time determined in the same solution during electrolysis with a symmetrically alternating current. Comparison of Curves 1 in Figures 2 and 3 with the curve in Fig. 4 shows that the absolute values of the anodic and cathodic polarizations fall considerably when alternating current is used. The explanation of this lowering of the polarization is that the impoverishment of the electrode surface layer during the separation of silver is succeeded by its enrichment during the [illegible] of silver. As a result both the cathodic and the anodic polarizations are lowered.

Fig. 5 shows polarization curves determined by the rapid method [5] in the same solution at the maximum [illegible] ma/sq.cm. Curve 1 was taken at a rate of 0.416 cm/sec. One period of this curve, i.e. the [illegible] time for which the electrode acted as anode and the time for which it acted as cathode, was 30 seconds. Curve 2 was taken at a rate of 4.166 cm/sec, and the durations of the cathodic and the anodic polarizations were [illegible]. Curve 3 was taken at a rate of 12.5 cm/sec, and the duration of one period was one second. [illegible] from these curves the absolute values of the cathodic and anodic polarizations and the form of the curves depend on the rate at which the determinations were made. When they were made at a low rate [illegible] the anode curve had quite a different appearance, and differed from the cathode curve by the [illegible] characteristic "steps", the physical significance of which will be examined below.

Fig. 6 shows the variation of cathodic and anodic polarizations with time in electrolysis with alternating current [illegible] ma/sq.cm. The curve shows that the limiting value of the cathodic polarization is attained after 3 [illegible] and as the value of [illegible] mv, at the same time vigorous evolution of hydrogen occurs. When the direction of

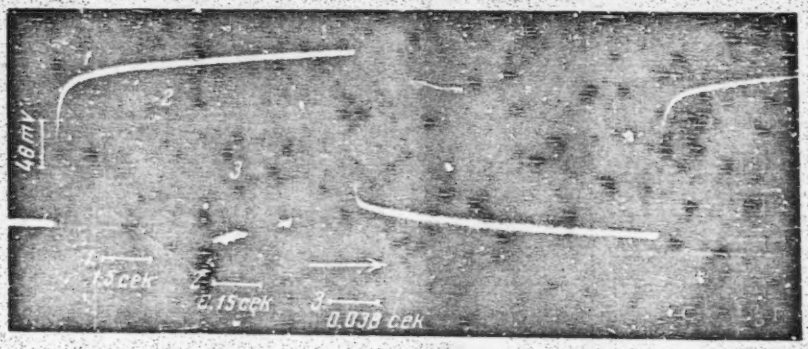


Fig. 2. Variation of cathodic polarization with time ("cek" = sec.)

Fig. 3. Variation of anodic polarization with time ("cek" = sec.)

Fig. 4. Variation of polarization with time during electrolysis with alternating current. ("sec" = sec.)

Fig. 5. Polarization curves taken by the rapid method at a maximum current density of 50 ma/sq. cm.

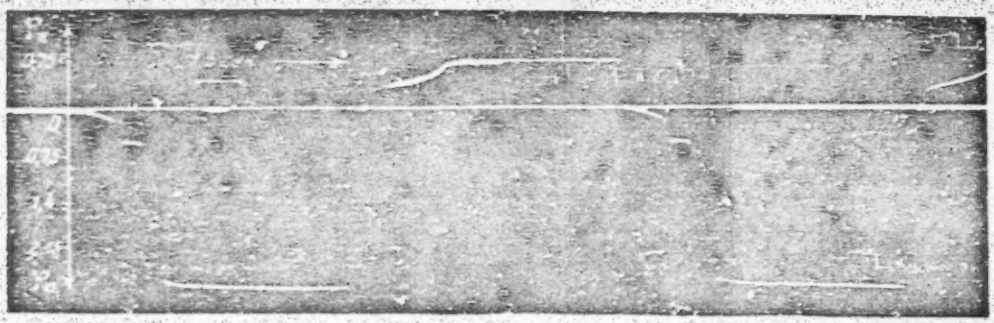

Fig. 6. Variation of polarization with time during electrolysis with alternating current.

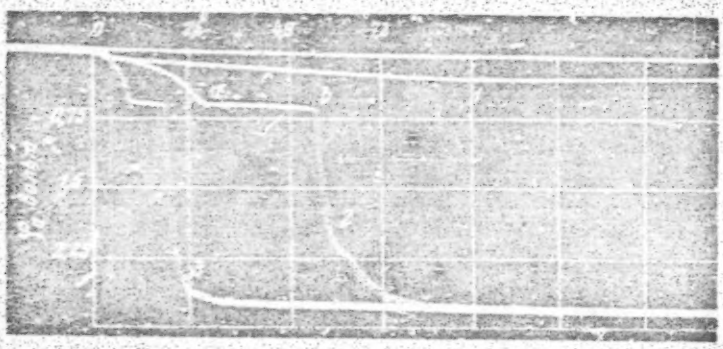


Fig. 7. Variation of anodic polarization with time.

the current is reversed, the passivation of the electrode is brought about in 2.15 seconds. The next reversal of current removes the anodic passivity, and the above-described process is repeated. When, however, the duration of deposition and dissolution of silver is diminished, conditions may be attained under which the cathodic and anodic polarizations cannot attain their limiting values.

Fig. 7 shows anodic-polarization curves taken at the same rate but at differing current densities. Curve 1 was taken at a current density of 10 ma/sq.cm, Curve 2 at 20 ma/sq.cm, and Curve 3 at 30 ma/sq.cm. On two of the curves there are characteristic plateaus. When the anodic polarization corresponds to the section Oa, the current is mainly consumed in dissolving silver with formation of complex cyanide ions. The point a corresponds to the beginning of passivation of the anode, i.e. the formation of a silver oxide film that prevents further dissolution:

$$2\,Ag + 2OH^- - 2e \rightleftarrows Ag_2O + H_2O$$

The plateau ab is generally found at a potential of 0.6 v relative to the potential of a silver electrode in the same solution. The length of ab diminishes as the current density increases, but the quantity of electricity spent in the formation of the oxide film remains almost constant and corresponds approximately to the formation of a monomolecular layer of silver oxide. The quantity of electricity depends only on the surface relief of the anode. At the point b the whole surface of the electrode is covered by an oxide film and there is a sharp rise in the anodic polarization, corresponding to further thickening of the oxide layer and separation of bubbles of oxygen.

Fig. 8 is the curve for the variation of anodic polarization with time during the dissolution of silver by means of an intermittent current. Over the section oc the electrode is polarized by a high-density current, which renders the anode passive. At the point c the current is switched off, and section df corresponds to the variation of the potential of the electrode when there is no current. In the curve for the fall in polarization in absence of current there is a sudden check (section de) at the same potential as that at which silver oxide forms, and this corresponds to the dissolution of the oxide film in potassium cyanide with formation of a complex silver cyanide.

$$Ag_2O + 4KCN + H_2O \rightleftarrows 2KAg(CN)_2 + 2KOH$$

The further slow fall in the potential along the section ef results from the levelling out of the concentrations of complex silver ions in the layer in immediate contact with the electrode.

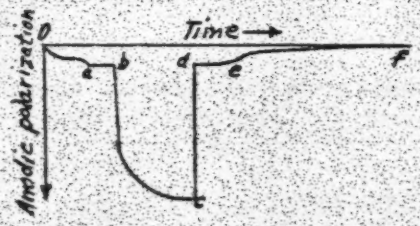


Fig. 8. Variation of anodic polarization with time during electrolysis with an intermittent current

Examination of the surface of the anode showed that at low current densities the silver dissolved with exposure of its structure. At high current density, when passivation of the anode occurred (Fig. 7, Curves 2 and 3), the surface of the silver was covered by a dark-colored oxide film; this had cracked in some places, and some of it had broken away as a result of internal strians and of mechanical disruption due to the separation of bubbles of oxygen. When the anode was polarized with an intermittent current, so that the oxide film was alternately formed and dissolved (Fig. 8), electrolytic polishing of the silver occurred.

## DISCUSSION OF RESULTS

Cathodic polarization during the deposition of metals can be the result of the slowest stage of one of the following processes: 1) formation and growth of crystals on the cathode; 2) slow discharge of ions; 3) slow decomposition of complex ions; and 4) slow delivery of discharging ions to the cathode.

The curves given above, which were determined during the deposition of silver from cyanide solutions, cannot be explained by the slowness of the formation of crystals, for, as has been pointed out in a number of investigations [6], when the process is retarded by electrocrystallization, the polarization is high only at beginning of the process and falls as the crystals forming at the cathode grow. However, the polarization curves obtained (Figs. 3, 4 and 6) show exactly the opposite picture of the variation of polarization with time, indicating that cathodic polarization must be due to other causes.

Again, the observed polarization during the deposition of silver from cyanide solutions cannot be explained by the slowness with which the complex ions are dehydrated and discharged, for, if the discharge were slow, the polarization would not vary, i.e. its value would remain constant with time.

The nonvalidity of explanations of the polarization based on the slowness with which complex silver cyanide ions are decomposed has been demonstrated fairly conclusively in some previous papers [7]. We consider that the slow rise of polarization with time and the great reduction in its value in electrolysis with alternating current (Fig. 1) can be explained by a) the slowness with which the discharging ions are delivered to the electrode* (concentrational polarization), and b) the slowness with which the discharging ions (in particular $Ag(CN)_2^-$) penetrate into the electrical double layer, i.e. the slowness with which they are adsorbed and the slowness of the process of displacing other ions and particles situated at the cathode surface.

Since the rate of the electrochemical reaction is determined by the concentration of the discharging anions adsorbed on the surface of the cathode, a lowering of the polarization will be observed, both when the current is periodically switched on and off (Fig. 2), and when the direction of the current is reversed (Fig. 4). The polarization is lowered to a particularly great extent when the direction of the current is reversed, for in the cathodic impulse the electric field is directed against the adsorption forces.

The picture that we have described of the variation of polarization with time can be interpreted as a kind of concentrational polarization, although this concept would need to be extended somewhat in content and sense. This polarization differs from the usual concentrational polarization in that the migration of ions is in the reverse direction and the concentration of the discharging ions at the electrode surface depends on the rate of adsorption, i.e. on the rate at which they penetrate the electrical double layer and on the rate at which they can displace other ions and foreign species from the cathode surface.

An examination of the changes in anodic polarization with time indicates that this also is concentrational and the way in which the anodic polarization changes at low current densities is analogous to the behavior of cathodic polarization, as can be seen from the curves in Figures 2 and 3. The fact that the polarization occurring during the deposition of silver from cyanide solutions is concentrational makes it possible to deposit with an alternating current and to use high current densities, without reaching the limiting values. As a result it is possible to improve the quality of cathode deposits.

As indicated above, when the anode is polarized by high current densities, it becomes passive (Figures 5, 6 and 7). In the literature [8] the passivation of silver in cyanide solutions has often been explained by the supersaturation of the layer in contact with the anode with the silver complex salt and its precipitation on the electrode surface as a viscous passivating film. We consider that this view is not fully substantiated in the present case, for it is impossible to explain, on its basis, the check in the fall in polarization (de, Fig. 8) when the current is switched off.

If the section ab corresponded to the crystallization of the complex silver salt on the anode, a smooth fall in potential with time should have been observed when the current was switched off. Actually, however, there was a check in the fall of the polarization when the current was switched off, and this was at the same potential as that at which the oxide was formed. The fact that the check in the rise of the polarization curve and the check in the fall of potential when the current was switched off were at the same potential level gives reason to suppose that the process occurring at the anode was the formation and dissolution of silver oxide and not the complex cyanide.

It should be noted in conclusion that it is usual in the examination of the mechanism of electrode processes to study the dependence of the value of the polarization on the current density, without taking into account the changes of polarization with time, in spite of the fact that in some cases these changes are very important for the understanding of the kinetics of the processes.

## SUMMARY

1. A simple method has been developed for the study of nonstationary electrode processes of short duration.

2. It has been shown that cathodic and anodic polarizations occurring during the deposition and dissolution of silver in cyanide solutions are essentially concentrational.

3. It has been shown that three sections can be distinguished in the curves for the variation with time of anodic polarization during electrolysis at high current densities, and that these correspond to the following processes: a) dissolution of silver with formation of complex cyanide ions, b) formation of a monomolecular layer of silver oxide on the electrode surface, and c) the further thickening of the oxide film and the evolution of free oxygen.

* The slow rise of the polarization with time cannot be explained by the charging current, since the current required for the charging of the electrical double layer is comparatively insignificant.

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# INTERHALOGEN COMPOUNDS AS COMPLEX-FORMERS*

Ya. A. Fialkov

Interhalogen compounds, i.e. compounds formed by one halogen with another, have for the main part received little study. Until very recently the information appearing in the literature on the properties of these compounds with the possible exception of iodine chloride, has been meager and sporadic and has not afforded a sufficiently complete characterization of this peculiar group of inorganic compounds, which are of great interest, both theoretical and practical. In the last two decades some previously unknown halogen fluorides have been prepared, the physical and chemical properties of the interhalogen compounds have been investigated in greater detail, and new ways have been found for their practical application. This activity has been accompanied by increased interest in this group of inorganic compounds.

Many of the peculiarities of the interhalogen compounds are to be attributed to the fact that they are formed from atoms of elements belonging to the same group and subgroup of Mendeleev's periodic system. The halogen subgroup differs from most of the other subgroups of the periodic system in that its members fairly readily unite with each other in pairs - each of the four halogens with the remaining three - with formation of substances varying in stability.

Eleven interhalogen compounds are now known, and these may be divided into four groups - $AB$, $AB_3$, $AB_5$, and $AB_7$ - according to the numbers of the halogens, and also into three groups - either as the halides of chlorine, bromine, and iodine, or as the halogen fluorides, chlorides, and bromides - according to chemical composition. The classification of the interhalogen compounds is given in Table 1.

TABLE 1

Classification of Interhalogen Compounds

| Main groups of interhalogen compounds | $AB$ | $AB_3$ | $AB_5$ | $AB_7$ |
|---|---|---|---|---|
| Chlorine fluorides | $ClF$ | $ClF_3$ | – | – |
| Bromine fluorides | $BrF$ | $BrF_3$ | $BrF_5$ | – |
| Iodine fluorides | – | – | $IF_5$ | $IF_7$ |
| Bromine chlorides | $BrCl$ | – | – | – |
| Iodine chlorides | $ICl$ | $ICl_3$ | – | – |
| Iodine bromides | $IBr$ | – | – | – |

Table 2 gives some of the physicochemical properties of the interhalogen compounds. The data in this table demonstrate the variety in the physicochemical properties of the interhalogen compounds (melting and boiling points, molecular state, conductivity, thermal stability), which is determined by the properties of the component halogens and valency state of the heavier halogen, the positively charged center of the molecule.

A discussion of the factors determining the physicochemical properties of the interhalogen compounds is outside the scope of this paper. We may remark however, that, apart from the factors mentioned above (the chemical nature and valency states of the halogens), the molecular structure of the compounds and effects associated with the screening of the central atom are also of great importance. The effect of the last factor, which reduces intermolecular association, is reflected particularly clearly in the values of the melting points and boiling points.

An examination of the data in Tables 1 and 2 prompts questions relating to the causes of the low thermal stability or nonexistence of certain interhalogen compounds corresponding both to high and to low valence forms of the halogens. These questions are most difficult to answer for the lower types of interhalogen compounds such as $AB$ and $AB_3$, the stabilities of which fall in the fluoride series in the order of chlorine, bromine, and iodine fluorides; in the series of bromine and iodine fluorides the stability increases as we pass from the lower ($AB$) to the higher forms ($AB_5$ and $AB_7$), and for iodine it has not been found possible to prepare the mono- and tri-fluorides. If and $IF_3$, while $BrF_5$, $IF_5$, and $IF_7$ are among the most stable of the interhalogen compounds. For the reasons given above we cannot discuss these and related matters here, but it may be pointed out that similar phenomena are known for the fluorides of elements in some of the other subgroups of the periodic table.

The interhalogen compounds, particularly those of type $AB$, show similarities to the halogens themselves in

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their physical and chemical properties, as pointed out long ago by D. I. Mendeleev when examining the properties of iodine chloride and trichloride [1].

TABLE 2

Some Physical Properties of Interhalogen Compounds

| Formula | M.p. (°C) | B.p. (°C) | State at room temperature | Electrical conductivity at the melting point ($ohm^{-1} \cdot cm^{-1}$) | Trouton's constant | Density at the boiling point | Degree of dissociation in the vapor phase at 25° (%) |
|---|---|---|---|---|---|---|---|
| ClF | −155.6 | −100.1 | Gas | | 28 | 1.62 | $1.2 \cdot 10^{-7}$ |
| $ClF_3$ | − 82.6 | 12 | Gas | $3 \cdot 10^{-8}$ (at 0°) | 20.8 | 1.8495 | 5.2 * |
| BrF | ~−33 | ~20 | Liquid | | 20.5(?) | | Very high (complete at 50°) |
| $BrF_3$ | 8.8 | 127 ± 1 | Liquid | $3.1 \cdot 10^{-3}$ | 25 | 2.51 | Very low |
| $BrF_5$ | 61.3 | 40.5 ± 0.5 | Liquid | | 23.7 | 2.41 | Insignificant** |
| $IF_5$ | 9.6 | 98 ± 1.6 | Liquid | $1.6 \cdot 10^{-5}$ | 27.2 | | Insignificant*** |
| $IF_7$ | 5–6 | 4.5 | Gas | | <26.4 | 2.80 | Insignificant**** |
| BrCl | From about −66 to −54 | Near to room temperature | Gas | | | | 21 |
| $Cl_2$ α | 27.2 | 100–102 | Solid | $4.60 \cdot 10^{-3}$ | 26.7 | | 0.38 |
| $Cl_2$ β | 13.9 | | | | | | |
| $Cl_2$ | 101 (at 16 atm) | Decomposes | Solid | $8.5 \cdot 10^{-3}$ | | | complete |
| Br | 42 | ~166 | Solid | $4.0 \cdot 10^{-4}$ | | | 8.8 |

* This value is that of the degree of association of $ClF_3$ at 1 atm.

** Bromine pentafluoride is stable at least up to 460°.

*** Iodine pentafluoride begins to decompose only above 400°.

**** Iodine heptafluoride is stable at least up to 500°.

The interhalogen compounds also show definite differences in chemical properties from the free halogens from which they are formed. These peculiarities are to be attributed to the polar character of their molecules and their higher polarizability, to the electropositive character of one of the component halogens, and to the electrodissociation of many of them with the formation of positively and negatively charged halogen ions. These peculiarities of interhalogen compounds determine their high reactivity in various reactions*, including complex forming reactions.

The principal chemical properties of interhalogen compounds are as follows.

1. They are powerful oxidizing agents for various inorganic and organic substances.

2. When they react with various inorganic substances - oxides, salts, and others - they form the corresponding simple or complex halides. These reactions, which often have very complicated mechanisms, are partially of an oxidation-reduction type.

3. Some interhalogen compounds (ICl, IBr, BrCl, and others) are able to add at multiple bonds in unsaturated organic compounds.

4. They are able to halogenate organic compounds (phenols, amines, etc.) by replacement of hydrogen by halogen.

5. They combine with nitrogenous and oxygenous organic bases, and similar compounds with formation of complex compounds of the type

* Halogen fluorides, for example, are often more reactive than chlorine or fluorine separately.

$C_5H_5N \cdot ICl$[2,3]; $C_5H_5N \cdot 2ICl$[3]; $C_4H_8O_2 \cdot ICl$[4]; $C_4H_8O_2 \cdot IF_5$[5]; $C_5H_5N \cdot ICl_3$, $C_5H_{11}N \cdot ICl$[6,7]; etc.

6) They form complex (so-called double) halides with the halide of other elements, for example:

$KCl \cdot ICl$[8,9]; $PCl_5 \cdot ICl$[10,11]; $PBr_5 \cdot IBr$[12]; $SbF_3 \cdot KF$, $BrF \cdot SbF_5$[13]; $KF \cdot IF_5$[14].

Even this incomplete list of the types of chemical reactions that can be effected with the aid of interhalogen compounds will indicate the possible significance that this group of inorganic compounds can have in chemical practice, in particular the chemistry of complex compounds.

The nature of the solvent has a great effect on the behavior of interhalogen compounds in chemical reactions. The effect of the solvent is manifested in the following ways:

1. Solvation of interhalogen molecules, and the ions that they form, by the molecules of polar solvents.

2. Polarization of interhalogen molecules. Thus, the dipole moment of iodine chloride in the gaseous state is 0.65 D [15], and increases when the compound is dissolved in carbon tetrachloride or cyclohexane to 1.48 D[16]. The additional polarization of interhalogen molecules under the action of the solvent can lead to a considerable increase in the ionic character of the bond $Hal^{I}-Hal^{II}$.

3. Finally, the solvent may affect the way in which the interhalogen compound dissociates: not only does thermal dissociation occur with formation of halogen molecules, but also electrolytic dissociation. For iodine chloride the equilibria can be represented as follows:

$$I_2 + Cl_2 \rightleftarrows (ICl)_2 \rightleftarrows I^+ + ICl_2^- \rightleftarrows 2I^+ + 2Cl^-.$$

Increase in the polar character of the solvent (increase in dipole moment and, particularly, dielectric constant) will create, as a result of processes indicated above, conditions favorable for a shift in the equilibrium in the direction of an increase in the concentration of ions* in the solution. Such solutions, therefore, will conduct an electric current.

Interhalogen compounds are very interesting ... their relation to the chemistry of complex compounds. Their intermediate state between nonpolar halogens and highly polar halides, their variety in composition and chemical properties, and their comparatively high polarizabilities create the possibility of studying well-defined manifestations of a very important factor in processes of complex formation, namely, the mutual polarization of the reaction components, as observed for complex compounds having a nonmetallic central atom. As is well known complex compounds of this type have been prepared in smaller numbers and have been investigated to a much less extent than complexes in which the central atom is derived from a metal ion.

A comparative study of complex-forming reactions in which halogens or interhalogen compounds take part would also be of great interest. Until recently, however, only a few complex compounds formed by interhalogen compounds were known, their structures were obscure, and their place in the system of classification of complex compounds was uncertain.

The main object of this paper is the examination of these and other similar matters on the basis of data from the literature and the results of investigations carried out by the author with the collaboration of Kuzmenko, Kuzyka, Kaganskaya, Shor, Abarbarchuk, and others at the Institute of General and Inorganic Chemistry of the Academy of Sciences of the Ukrainian SSR.

The complex compounds formed by interhalogen compounds may be devided broadly into two groups:

1. Addition compounds formed with nitrogenous, oxygenous, and similar organic bases (see above).

Complex compounds of this group include compounds that vary greatly in stability, from solvates of variable composition occurring in a state of dissociation in solution through various intermediate forms, to highly stable complexes, which do not decompose even when heated above their melting points.

A study of these interhalogen complex compounds is of great interest also for the theory of solutions. In the more stable compounds of this type there is a coordinate link. Such a link may be formed when the interhalogen compound dissociates into ions owing to the polarization of its molecules by the solvent. The resulting positively charged halogen ions add as electron acceptors to oxygen, nitrogen, or similar electron-donating atoms in the molecules of the organic base. This process results in the formation of complex cations of the onium type, for example:

$$C_5H_5N + I^+ + Cl^- \rightarrow [C_5H_5N \rightarrow I]^+ Cl^-$$

* solvated by solvent molecules

or

$$C_5H_5N + I^+[ICl_2]^- \longrightarrow [C_5H_5N{-}I]^+[ICl_2]^-$$

This concept of the nature and structure of the ions yielded by such halogen and interhalogen complex compounds was advanced by us [1-3] with the object of explaining phenomena observed during the electrolysis of these compounds (or solutions of iodine halides ICl, IBr, and $ICl_3$ in polar organic solvents): both halogens - iodine and chlorine or iodine and bromine - were finally (when electrolysis was sufficiently prolonged) transferred to the anode*, although during electrolysis the ratio I/Cl or I/Br increased in the cathode department and diminished in the anode department. The molecules of the organic substance were transferred to the cathode.

On the basis of data in the literature and the results of the author and Muzyka, we have proposed the following scheme of the electrode processes:

a) Anode process: $2Cl^- - 2e = Cl_2$

b) Cathode process: $2[R{-}I]^+ + 2e = 2R + I_2$.

The iodine molecules liberated at the cathode undergo cathodic reduction, $I_2 + 2e \rightarrow 2I^-$, and the resulting iodide anions are then transferred to the anode. Hence, as shown by the author with Kaganskaya [9] and Muzyka [3] for the electrolysis of the systems $C_5H_5NO_2$–ICl and $C_5H_5N$–ICl, at first AgCl is deposited on the silver anode, but later also AgI is deposited.

The cathodic reduction of iodine during the electrolysis of aqueous and nonaqueous solutions of polyiodides has been proved by Shevchenko [18].

The formation of a coordinate link in molecular compounds formed by halogens and by interhalogen compounds with organic substances has been shown also in a series of investigations carried out at Leningrad University by Shukarev, Lilich, and others [19-20]. Lilich and Preminkova [22] made calculations, based on spectrophotometric measurements, of the equilibrium constants (stability constants) of molecular compounds formed by bromine, iodine, iodine chloride, and iodine bromide with dioxan and methanol. The thermal stabilities of these complexes increase in the order $Br_2 < I_2 < IBr < ICl$, i.e. in the order of increased asymmetry of the distribution of outer electrons in the halogen or interhalogen molecule. The stabilities of these molecular compounds increase also as the electron-donating properties of the organic "bases" increase**, for a given electron acceptor. The presence of a coordinate link in the compound $C_5H_5N$–ICl has been confirmed also by the work of Sheka [23], who established the formation of an ion-molecular complex in the system $C_5H_5N$–ICl in chloroform solution on the basis of measurements of the deviations of the values of dielectric constant and polarization in this system from their additive values.

An examination of the literature shows that the molecular compounds between interhalogen compounds and organic substances are formed almost entirely by the addition of ICl, IBr, or, rarely, $ICl_3$ to various aliphatic and aromatic compounds. Thus, in view of this fact Fialkov and Muzyka have investigated the reaction of iodine monochloride with amides, the molecules of which contain two different electron donors, the nitrogen atom

$$R{-}C(=O){-}NH_2$$

and the oxygen atom.

[illegible] demand extensive application of methods of physicochemical analysis.

[illegible] directions of development can be distinguished in the investigation of the chemistry of complex compounds. The first consists in the investigation of systems that for practical purposes are nonequilibrium systems, i.e. systems in which the position of equilibrium is almost completely displaced in the direction of the formation of stable complex compounds that may be separated comparatively easily and at the same time almost quantitatively from the system. Investigations on such complex compounds, e.g. platinum compounds, are characterized by the predominant use of preparative methods, i.e. the synthesis of the complex compound to prove that complex formation occurs, followed by the establishment of the composition, structure, and properties of the complex by the methods of chemical analysis and of physical chemistry.

The second of these directions consists in the investigation of systems in which comparatively unstable complex compounds are formed. In the investigation of these systems the method of physicochemical analysis, so brilliantly developed in our country by Kurnakov and his school, has acquired extreme importance.

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* When silver anodes were used, a deposit of the corresponding silver halides was formed on their surfaces.

** Compounds formed with dioxan are more stable than those formed with methanol.

Equilibrium systems, and the unstable complex compounds that are formed in them, are of considerable interest, partly because they are so common, and partly because they comprise an intermediate field between the systems that, for practical purposes, are nonequilibrium systems, and solutions. These systems include most of the systems in which complex compounds are formed between interhalogen compounds, in particular iodine halides, and organic bases of halides of other elements.

In the Complex Compounds Laboratory of the Institute of General and Inorganic Chemistry of the Academy of Sciences of the Ukrainian SSR, systems containing compounds of iodine halides, and, in fact, equilibrium systems in general, are investigated by a combination of several methods of physicochemical analysis in order to detect complex compounds and determine their compositions, and this is followed by the isolation (synthesis) of individual compounds and their investigation with the aid of chemical analysis and of physicochemical methods, including, when possible, electrochemical methods. The experience gained in our laboratory has shown that such a combination of methods of investigation enables complex compounds to be studied from all angles and enables us to obtain conclusive results concerning their presence, compositions, properties, and structures.

As a result of such investigation on systems consisting of iodine chloride and acetamide $CH_3CONH_2$ [24], benzamide $C_6H_5CONH_2$ [25], and NN-diethylbenzamide $C_6H_5CON(C_2H_5)_2$ [26], and also on the systems IBr–$C_6H_5CONH_2$ [27] and ICl–$C_5H_5N$ [3], it was found possible to prepare a number of complex compounds not previously described in the literature, or to establish their formation in the liquid phase and determine some of their physicochemical properties and the nature of the ions present, etc.

It was shown that in such systems complexes of four types are formed:

1. Compounds of the type R·IX: $CH_3CONH_2 \cdot ICl$; $C_6H_5CONH_2 \cdot ICl$; $C_6H_5CONH_2 \cdot IBr$; $C_5H_5N \cdot ICl$; $C_5H_5N \cdot IBr$.
2. Compounds of the type R·2IX: $C_5H_5N \cdot 2ICl$.
3. Compounds of the type 2R·IX: $2CH_3CONH_2 \cdot ICl$.
4. Compounds of the type $(R \cdot IH)_2$: $(C_6H_5CONH_2 \cdot ICl)_2$.

On the basis of results obtained from the study of ion transfer and certain other data the following structures are suggested for complex compounds of these types:

1. For R·IX: $\left[\text{C}_5\text{H}_5\text{N}^+\text{–I}\right]\text{Cl}$; $[C_6H_5CONH_2 \cdot I]Br$,

2. For R·2IX: $\left[\text{C}_5\text{H}_5\text{N}^+\text{–I}\right][ICl_2]$.

3. For 2R·IX: $\left[\begin{matrix}\text{CH}_3\text{–CONH}_2 \\ \text{I}^+ \\ \text{CH}_3\text{–CONH}_2\end{matrix}\right]\text{Cl}$.

4. For $(R \cdot IX)_2$: $\left[\begin{matrix}\text{C}_6\text{H}_5\text{–CONH}_2 \\ \text{I}^+ \\ \text{C}_6\text{H}_5\text{–CONH}_2\end{matrix}\right][ICl_2]$.

In compounds of the last two types the $I^+$ ion forms a covalent bond, as an electron acceptor, with one amide molecule, and a bond with the other molecule that probably results from polarization or Van der Waals interaction.

The structure of the cation $[(C_6H_5CONH_2)_2I]^+$ can be compared with that of the so-called "anomalous" ammonium salts, for example $[2NH_3 \cdot H]Cl$.

In considering the structure of compounds formed by iodine halides with amides we must remember that carboxylic amides can be represented by two tautomeric formulas, for example:

$$\text{CH}_3\text{–C}\begin{matrix}\text{O} \\ \text{NH}_2\end{matrix} \rightleftharpoons \text{CH}_3\text{–C}\begin{matrix}\text{OH} \\ \text{NH}\end{matrix}$$

It was found that NN-diethylbenzamide $C_6H_5CON(C_2H_5)_2$, which cannot undergo tautomeric rearrangement, reacts with iodine chloride with formation of an equimolecular compound having similar properties to that of the

analogous compound derived from unsubstituted benzamide. We may infer from this that amides react with iodine chloride and iodine bromide in the first (amide) form of the two shown above. As regards the question of which electron donor - the nitrogen or the oxygen - participates in the link between the amide molecule and the $I^+$ ion, these investigations do not yet provide an answer.

II. The second group of complex compounds formed by interhalogen compounds contains addition compounds formed by bromine and iodine halides with the halides of other elements or the halides of complex inorganic or organic cations (see early part of paper).

Many of these complex compounds, which belong to the class of double halides, are considerably more stable than the original bromine and iodine halides. Also, they are so active chemically that they may be successfully applied for various purposes - for oxidation reactions, and for the halogenation, in particular fluorination, of inorganic and organic substances, etc.

The formation of complex compounds of this group, their compositions, and the nature of the ions that they yield are again (as for compounds of the first group) closely dependent on the electrolytic dissociation of the interhalogen compounds themselves. Their Trouton constants (Table 2) and other data show that interhalogen compounds are associated in the liquid state and in some solvents. For their dimeric molecules the ionization process can be represented as follows:

$$(ICl)_2 \rightleftarrows I^+ + ICl_2^- \quad [28, 9]$$
$$(BrF_3)_2 \rightleftarrows BrF_2^+ + BrF_4^- \quad [29, 30]$$
$$(IF_5)_2 \rightleftarrows IF_4^+ + IF_6^- \quad [30]$$

Hence, when interhalogen compounds react, in the melted condition or in solution, with halides of other elements, complex halides of two types may be formed: the interhalogen compounds may form a cation, or may enter into the composition of a complex anion. In fact, when the data in the literature and the results of the researches of the Institute of General and Inorganic Chemistry of the Academy of Sciences of the Ukrainian SSR on the compositions and structures of complex compounds formed by bromine and iodine halides with the halides of other elements are generalized, it is found that such complexes can be divided into "cationic" and "anionic". Examples of such complexes are given in Table 3.

TABLE 3

Cationic and Anionic Complexes formed by Bromine and Iodine Halide with Halides of other Elements

| Interhalogen compound | Cationic complexes | Anionic complexes |
|---|---|---|
| ICl | $[IAsCl_4]\cdot ICl$ | $K[ICl_2]$ |
| | $[SbCl_4]\cdot nICl_3$ | $[PCl_4][ICl_2]$ |
| | $n = 1$ and 2 | |
| | $[SbCl_4]\cdot nICl_3$ | |
| | $n = 3$ and 4 | |
| IBr | $[AlBr_4]$ | $K[IBr_2]$ |
| | | $[PBr_4][IBr_2]$ |
| $BrF_3$ | $[BrF_2][SbF_6]$ | $K[BrF_4]$ |
| | $[BrF_2]_2[SnF_6]$ | $Ba[BrF_4]_2$ |
| | $[BrF_2][SO_2F]$ | $Ag[BrF_4]$ |
| $ICl_3$ | | $K[ICl_4]$ |
| | | $H[ICl_4]\cdot 4H_2O$ |
| $IF_5$ | $[IF_4][BF_4]$ | $K[IF_6]$ |
| | $[IF_4][SbF_6]$ | |

These complex compounds, both cationic and anionic, can be prepared by direct reaction with halides in melts or solutions. Some indirect methods are also known for the preparation of such complex compounds. These are based mainly on oxidation reactions, e.g. the action of iodine on $PCl_5$ or $PBr_5$, which proceeds as follows ($X = Cl$ or $Br$):

$$PX_5 + I_2 \rightleftarrows PX_3 + 2IX$$
$$2PX_5 + 2IX \rightleftarrows 2[PX_4][IX_2]$$
$$3PX_5 + I_2 \rightleftarrows 2[PX_4][IX_2] + PX_3 \quad [21, 32, 31]$$

Among the compounds given in Table 3 there are some double halides having an iodine cation, which were first prepared or investigated at the Institute of General and Inorganic Chemistry of the Academy of Sciences of the Ukrainian SSR (Fialkov [32], Kaganskaya [33], Sher [33], Abarbanik [34]*), and there are also some compounds having a tetrahalophosphonium cation, the structures of which were established by the author in collaboration with Kazarnovskii [13, 12, 21]; these belong to a new class of complex compounds having a complex "acidocation" [28], in which the central atom is of a metalloid.

Complexes containing the difluorobromonium $BrF_2^+$ and tetrafluoroiodonium $IF_4^+$ cations belong to the same general class of complex compounds. These double halides, and also compounds having the complex anions $BrF_4^-$ and $IF_6^-$

*) Earlier previously known compounds of this type were $SbCl_5 \cdot 2ICl$ and $SbCl_5 \cdot 3ICl$, which were discovered by Ruff and co-workers [35, 36]. There is no information about the nature of these compounds in Ruff's papers.

were prepared by Emeleus and his coworkers [30, 38].

Interhalogen compounds—in that they enter into the compositions of both cationic and anionic complexes, now forming the cation, and now the anion of double halides—have a dual function (a peculiar "amphotericity"**), for example:

$$ICl + C_5H_5N \rightarrow [C_5H_5N{-}I] + Cl^-;$$

$$ICl + PCl_5 \rightarrow [PCl_4]^+ + [ICl_2]^-;\quad AlCl_3 + ICl \rightarrow I^+ + [AlCl_4]^-;$$

$$BrF_3 + KF \rightarrow K^+ + BrF_4^-;\quad SbF_5 + BrF_3 \rightarrow BrF_2^+ + SbF_6^-.$$

The fact that $PCl_5$ and $SbCl_5$ form complexes of different types with iodine chloride—$[PCl_4][ICl_2]$ and $[SbCl_4]$ (see Table 3)—is to be explained by their difference in structure and polarizability [42]. As is well known, $PCl_5$ and $SbCl_5$, in the form of separate molecules, both have the structure of a trigonal bipyramid, but whereas $PCl_5$ forms a crystalline lattice consisting of tetrahedral cation $[PCl_4]^+$ and octahedral anions $[PCl_6]^-$ and can react with various substances in the form $[PCl_4]Cl$, e.g. $[PCl_4]Cl + ICl = [PCl_4][ICl_2]$, such properties are not possessed by antimony pentachloride.

It is interesting also to note the differing behaviors of $PCl_3$, $AsCl_3$, and $SbCl_3$ toward iodine chloride. $PCl_3$ is readily oxidized by iodine chloride, forming first $PCl_5$, and the $[PCl_4][ICl_2]$ [8]. $SbCl_3$ is not oxidized, but it combines with ICl. $AsCl_3$, however, as Abarbarchuk showed [43], does not react at all with iodine chloride: it is neither oxidized by it, nor does it combine with it. These facts are to be explained by the differences in the reducing properties of $PCl_3$, $SbCl_3$, and $AsCl_3$ and by the steric factor—the relations between the ionic radii.

The data that we have given confirm the great and varied scientific interest that the interhalogen compounds have for the chemistry of complex compounds. The practical application of the interhalogen compounds and the complex compounds that they form is based on their high reactivities and the variety of their chemical properties. Halogen fluorides are already being used for the fluorination of inorganic and organic compounds and for the preparation of the complex fluorides of various elements. The high activity of halogen fluorides as fluorinating agents, which is often equal to or greater than that of fluorine, is in some cases to be explained by the formation of more or less stable complex fluorides by the action of the halogen fluorides on inorganic substances. For example, complex fluorides of the type $M(RF_n)_m$ may be obtained by the action of $BrF_3$ on a mixture of a halide or oxyacid salt of the given cation and the stoichiometric amount of a halide or oxide of the element that is to form the central atom of the complex. In this way the preparation has been effected of, for example, hexafluoniobates, hexafluotantalates [44], fluopalladates, fluoplatinates [45], and similar complexes.

The fluorinating action of $BrF_3$ has been described in greatest detail [38]. $BrF_3$ is preferred for this purpose because the reaction can be carried out in the liquid phase at room temperature. The reaction is often quantitative. When reaction tends to be violent, it can be moderated by addition of dry bromine to the reaction mixture. Obstacles to the wide practical application of $BrF_3$ are its toxicity and its action in producing severe burns, similar to those caused by hydrogen fluoride.

As a second example of complex compounds of interhalogen compounds which are used in practice we must mention the complex acid $H[Cl_2]$ and $H[Cl_4]$, which are contained in hydrochloric acid solutions of ICl and $ICl_3$, respectively. Such solutions can be readily prepared by the action of hydrochloric acid on stoichiometric amounts of KI (or iodine) and $KIO_3$. When there is a certain excess of hydrochloric acid, these solutions are very stable. In hydrochloric acid solution these complex acids are in equilibrium with their dissociation products, which include $I^+$ ions.

Gengrinovich, who carried out the first investigations in this field, Shakh. Kagan [46-51] and others, working in the author's laboratory and in other institutes, have developed numerous methods for the quantitative volumetric determination of inorganic and organic substances based on oxidation, replacement, double-bond addition, and complex-forming reactions of iodine derivatives of organic substances, and also on methods for the preparation of these substances. The reactions proceed quantitatively, and very pure products are obtained, contamination with chlorine-substituted products being negligible.

There is every reason to suppose that interhalogen compounds and the complex compounds derived from them will find a much wider application in practice. It is therefore necessary to intensify investigation on the chemistry of the complex compounds of interhalogen compounds both preparative and physicochemical.

** This peculiarity of interhalogen compounds brings the investigations in this field close to the problem of acid-base interaction [39, 40, 41].

## SUMMARY

1. Investigations of interhalogen compounds and the complex compounds that they form have made it possible to establish the structures of many such complex compounds, their chemical properties, and the nature of the ions that they form.

2. Double halides have been prepared in which iodine is present as a cation.

3. The field of complex compounds in which the central atom is a nonmetal has been extended.

4. It has been shown that complex compounds containing "acidocations" having a metalloid as central atom are found more frequently than was previously thought.

5. Some generalizations have been made regarding the relation between the chemical properties and structure of complex compounds and the structures and polarizabilities of the original interhalogen molecules.

6. Some new ways have been found for the practical application of iodine halides ($ICl$ and $ICl_3$), for the quantitative determination of inorganic and organic substances, and for the preparation of iodine derivatives.

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# ACTION OF SULFURIC ACID ON 2-METHYLTHIOPHENE

V. M. Rodionov* and E. F. Polunina

As an examination of the literature will show, the sulfonation of thiophene has been studied fairly thoroughly. When thiophene is treated in the cold with concentrated sulfuric acid in presence of a large amount of an indifferent solvent, the main product is 2-thiophenesulfonic acid, and a small amount of 2,2'-bithiophene is obtained as by-product [1]. The sulfonation of thiophene homologs under the same conditions proceeds more vigorously and is accompanied by much resinification, and the resulting mixture of sulfonic acids and products arising by polymerization, condensation, and oxidation is difficult to separate [2].

Sulfonic acids of thiophene homologs have generally been prepared by double decomposition between acetyl derivatives of the parent compounds and concentrated sulfuric acid. Recently, pyridine-sulfur trioxide and dioxan-sulfur trioxide have been successfully applied for the sulfonation of thiophene and other acidophobic heterocyclic compounds [3]. Although the direct sulfonation of thiophene homologs has lost much of its importance since the development of improved methods of preparing sulfonic acids, the study of processes occurring when sulfuric acid reacts with thiophene homologs is of more than theoretical interest. Thus, this process lies at the basis of the manufacture of ichthyol, a medicinal prepared by the sulfonation of shale tar distillates rich in thiophene derivatives.

In our work on the improvement of the quality of ichthyol [4] and the preparation of the medicinal albichthyol, which can replace ichthyol and is more effective [5], it became necessary to study the side reactions accompanying sulfonation of thiophene derivatives. In view, however, of the great difficulties presented by the isolation of individual substances from the mixtures obtained by the sulfonation of shale tar distillates, we decided to investigate the sulfonation of individual thiophene derivatives - in the first place 2-methylthiophene, prepared synthetically. In the present investigation we have studied the following factors: amount and concentration of sulfuric acid, temperature, and duration of reaction.

The reaction was carried out in presence of petroleum ether (5 : 100). When 2-methylthiophene was sulfonated under conditions close to those used in the manufacture of ichthyol (slightly fuming sulfuric acid containing about 0.5% of free sulfur trioxide; temperature 55-50°; duration of reaction 30 minutes), there was copious evolution of sulfur dioxide, and much resinification occurred.

No individual substance could be isolated from the resin. When the temperature was lowered to 25-30° and the duration of the reaction was reduced to 2.5-3 hours, a new sulfonic acid was isolated from the sulfonation products. This substance differed greatly from the known sulfo derivatives of 2-methylthiophene, its salts even the alkali-metal salts, having very low solubilities. The highest yield of this sulfonic acid was obtained when monohydrate was used and a small change in the acid concentration in one direction or the other resulted in a reduction of yield (see the table). The crude sulfonic acid was obtained as a reddish-brown syrupy liquid. It was not found possible to isolate the free sulfonic acid in the pure state: it was highly soluble in water like the mono- and di-sulfonic acids of 2-methylthiophene, did not crystallize out from acid solutions, and could not be prepared by double decomposition of its lead salt with hydrogen sulfide, since its lead salt, unlike those of the known sulfonic acids of 2-methylthiophene, was completely insoluble in water.

The new sulfonic acid gave potassium, sodium, ammonium, and p-toluidine salts of low solubility at ordinary temperature, and its barium and lead salts were almost insoluble even at high temperatures. The elementary composition of the sulfonic acid was established by the elementary analysis of its ammonium and sodium salts and by analysis of the barium salt for barium and the p-toluidine salt for nitrogen. The molecular weight of the last salt was determined by the Rast method. The results of these determinations showed that the new sulfonic acid contained one sulfo group in its molecule and had a molecular formula of $C_{15}H_{14}S_4O_3$. We did not succeed in characterizing the sulfonic acid by means of its acid chloride or amide.

As a result of numerous experiments it was shown that reaction between the sodium salt of the sulfonic acid and phosphorus pentachloride proceeds readily in presence of absolute benzene at 40-45°, and that the product is soluble in benzene, but it was found impossible to isolate the substance from benzene because of its instability: as soon as benzene was removed, it resinified. Attempts to prepare the amide from the benzene solution

* Deceased

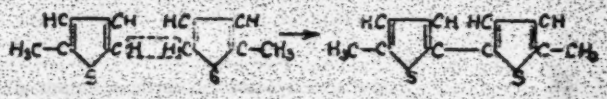
TABLE

| No. | Amount of crude ribophosphate (g) | petroleum ether (ml) | $H_2SO_4$ (g) | Density or concentration | Reaction temperature (°C) | Amount of ammonium salt (g) | Yield of ammonium salt (%) |
|---|---|---|---|---|---|---|---|
| 1 | 5 | 100 | 100 | 1.849 (20°) | 25-30 | 0.1 | 1.5 |
| 2 | 5 | 100 | 100 | 1.840 (20°) | 25-30 | 0.7 | 10.6 |
| 3 | 4.6 | 100 | 90 | 1.839 (20°) | 25-30 | 1.2 | 20.2 |
| 4 | 10 | 200 | 200 | 1.838 (20°) | 25-30 | 4.75 | 36.0 |
| 5 | 7 | 150 | 150 | 1.838 (20.5°) | 25-30 | 2.5 | 27.3 |
| 6 | 10 | 200 | 200 | 1.837 (30°) | 25-30 | 2.6 | 19.7 |
| 7 | 4 | 80 | 80 | 99.51% | 20-30 | 1 | 18.9 |
| 8 | 9 | 300 | 180 | 99.36% | 20-30 | 0.9 | 7.6 |

Note: $H_2SO_4$ of density 1.839 (20°) has a concentration of 100% (monohydrate).

of the sulfonyl chloride were also unsuccessful. Treatment of the sulfonyl chloride with ammonia resulted in the formation of a light-yellow waxy substance, which could not be purified because it was insoluble in all of the usual solvents. The melting point of this substance could not be determined for, on being heated in a capillary, it sintered together and darkened in color.

Apart from the new sulfonic acid, a small amount of a solid substance was isolated from the unsulfonated resinous products. This substance, which crystallized from alcohol in the form of white plates melting at 63-66°, was of a neutral character and gave a positive reaction for sulfur and a not-altogether characteristic reaction for thiophenes with isatin and sulfuric acid. It was close in physical properties to 5,5'-dimethyl-2,2'-bithiophene, which was obtained synthetically by Steinkopf [6]. It is possible that this compound was formed by the oxidation of 2-methylthiophene by sulfuric acid, the reaction being analogous to that occurring in the sulfonation of thiophene and its chloro, bromo, and other derivatives:



In the sulfonation of 2-methylthiophene, apart from the above-described new sulfonic acid, other sulfonic acids were isolated in the form of their salts, which were readily soluble in water. Elementary analysis showed that they were mixtures of salts of mono- and di-sulfonic acids of 2-methylthiophene.

On the basis of our study of the composition of the new sulfonic acid we may make the following suggestions. The experimental conditions were favorable for reaction in the following three directions simultaneously: 1) sulfonation of 2-methylthiophene; 2) oxidative condensation with formation of bithiophenes and dithienylthiophenes; 3) sulfonation of the products of oxidative condensation. The structural formula of the new sulfonic acid may be represented tentatively: $C_4H_2CH_3S-C_4HCH_3S-C_4HCH_3S-SO_3H$.

## EXPERIMENTAL

### 1. Sulfonation of 2-Methylthiophene

A solution of 10 g of 2-methylthiophene in 200 ml of petroleum ether was placed in a flask fitted with stirrer, thermometer, dropping funnel, and reflux condenser. The solution was stirred mechanically, and 200 g of sulfuric acid, sp. gr. $1.838^{20°}$ (monohydrate), was added from the dropping funnel at such a rate that the temperature of the reaction mixture did not exceed 30°. When the whole of the acid had been added, the mixture was stirred for three hours, the temperature being maintained at 25-30°.

At the end of the reaction the mixture was poured carefully into 200 ml of ice water cooled from without with a mixture of ice and salt; petroleum ether separated (this should not give a reaction for 2-methylthiophene). The aqueous solution was shaken in a separating funnel with 100 ml of ether, and the mixture was allowed to settle. Three layers were formed: a) the top layer - an ether extract containing a small amount of sulfonic acids and resinous substances; b) the middle layer - a dark-colored syrupy liquid containing a mixture of sulfonic acids and also some aqueous sulfuric acid; c) the lower layer - a solution of sulfuric acid containing a small amount of sulfonic acids and resins.

The middle layer (about 20 ml), which contained products of the sulfonation of 2-methylthiophene, was dissolved in an equal volume of water, and the solution was neutralized with 10% aqueous ammonia. During this last process the color of the solution changed first from brown to green and then, at the neutralization point, to yellow. A finely crystalline precipitate of a difficultly soluble ammonium salt separated. The mixture was set aside for some hours to allow the precipitation to proceed to completion. The product was 3.65 g of dry salt, which was of a yellowish color. A further 0.9 g of the salt was isolated from the ether extracts. The total yield was 4.75 g, i.e. 36.9% calculated as $C_{15}H_{13}S_3-SO_3NH_4$.

The mother liquid contained a mixture of readily soluble ammonium salts of mono- and di-sulfonic acids of 2-methylthiophene. The ammonium salt of the sulfonic acid investigated was recrystallized three times from hot water. The pure salt crystallized in the form of fine white scales having a silvery reflex. It was readily soluble in alcohol, but insoluble in ether and in benzene.

Found %: N 3.52, 3.48; S 33.39, 33.14; C 45.87; H 4.09

$C_{15}H_{13}S_3-SO_3NH_4$. Calculated %: N 3.61; S 33.10; C 46.46; H 4.39

### 2. Preparation of the Sodium Salt and Investigation of its Composition

The mixture of sulfonic acids prepared by sulfonation of 10 g of 2-methylthiophene under the above-described

...chloride was dissolved in 20 ml of water, and the solution was neutralized with a 20% solution of sodium carbonate. A white precipitate of the difficultly soluble sodium salt separated. The mixture was set aside for some hours to allow precipitation to go to completion. The yield of the salt was 5.65 g, i.e., 42.3% calculated as

| | | |
|---|---|---|
| | Found %: | Na 5.70, 5.21; S 32.36, 32.53 |
| $C_{15}H_{13}S_2-SO_3Na$. | Calculated %: | Na 5.86; S 32.68 |

## 3. Preparation of the Barium Salt

The recrystallized ammonium salt (1 g) was dissolved in 400 ml of distilled water and the solution was heated to boil. Two or three drops of concentrated sulfuric acid were added, and then 4 ml of a 10% solution of barium chloride. A voluminous white precipitate formed.

When the mixture was cool, the precipitate was filtered off, washed free from excess of barium ions and dried to constant weight.

| | | |
|---|---|---|
| | Found %: | Ba 15.40, 15.46 |
| $C_{15}H_{13}S_2-SO_3\frac{Ba}{2}$ | Calculated %: | Ba 15.67 |

## 4. Preparation of the p-Toluidine Salt and Determination of its Molecular Weight

A solution of 0.4 g of p-toluidine in acetic acid was added to a solution of 1 g of the ammonium salt $C_{15}H_{13}S_2-SO_3NH_4$ in 100 ml of water heated to 50-60°. When the solution was cooled a voluminous white precipitate of the p-toluidine salt formed. The salt dissolved when warmed with water, alcohol, or benzene. It was recrystallized from water and then melted at 178-179°.

| | | |
|---|---|---|
| | Found %: | N 3.11 |
| $C_{15}H_{13}S_2-SO_3NH_3C_6H_4CH_3$. | Calculated %: | N 2.93 |
| | Found M: | 455.82; 471.15 (Rast's method) |
| $C_{15}H_{13}S_2-SO_3NH_3C_6H_4CH_3$. | Calculated M: | 477.43 |

## SUMMARY

1. When 2-methylthiophene is treated with sulfuric acid of specific gravity 1.838 (monohydrate) at 25-30° in the presence of an indifferent solvent (petroleum ether), a new sulfonic acid – a methyl[methyl(methylthienyl)thienyl] thiophenesulfonic acid – is obtained in a yield of 30% (isolated as ammonium salt) or 46% (isolated as sodium salt).

2. The ammonium, sodium, barium, and p-toluidine salts of this sulfonic acid have been prepared and the ...

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# REACTION OF ALKYL ORTHOTITANATES WITH TITANIUM TETRACHLORIDE IN A PIPERIDINE MEDIUM

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The reaction between alkyl orthotitanates and titanium tetrachloride (the reverse of disproportionation) is of interest for the synthesis of alkoxychlorotitaniums of general formula $(RO)_nTiCl_{4-n}$ ($n = 1, 2$, or 3), because alkyl orthotitanates are now fairly readily accessible. In the conversion of an alkyl orthotitanate into alkoxychlorotitaniums in this way, the total number of Ti–OAlk linkages in the products is the same as the number in the original alkyl orthotitanate.

According to the results of British chemists [1], reaction of an alkyl orthotitanate with a large excess of titanium tetrachloride yields an alkoxytrichlorotitanium. The authors were unable to isolate pure dialkoxydichlorotitaniums by the use of equimolecular amounts of reactants, and they concluded that mixtures of products containing different numbers of alkoxyl groups in their molecules were formed under these conditions. The authors did not attempt to obtain trialkoxychlorotitaniums by this method; their general conclusion was that the reaction between alkyl orthotitanates and $TiCl_4$ could be used only for the preparation of alkoxytrichlorotitaniums, for which purpose an excess of $TiCl_4$ was required.

In a previous paper [2] we stated that, by carrying out the reaction between alkyl orthotitanates and $TiCl_4$ taken in proportions corresponding precisely to the equations (I), (II), and (III) in a medium of benzene and petroleum ether at room temperature, we had obtained trialkoxychloro-, dialkoxydichloro-, and alkoxytrichlorotitaniums in high yields.

$$3(RO)_4Ti + TiCl_4 = 4(RO)_3TiCl, \quad (I)$$

$$(RO)_4Ti + TiCl_4 = 2(RO)_2TiCl_2, \quad (II)$$

$$(RO)_4Ti + 3TiCl_4 = 4ROTiCl_3 \quad (III)$$

It was found that dialkoxydichloro- and alkoxytrichloro-titaniums sometimes decomposed (underwent disproportionation) during vacuum distillation, so that it was better to purify these substances by recrystallization from benzene or from a mixture of benzene and petroleum ether.

We found that alkyl orthotitanates and trialkoxychloro-, dialkoxydichloro-, and alkoxytrichloro-titaniums formed crystalline double compounds with piperidine of composition $(RO)_nTiCl_{4-n}C_5H_{10}NH$, ($n = 1, 2, 3$, or 4). When the double compound of ethyl orthotitanate and piperidine was recrystallized and dried, it lost part of its piperidine, but the double compounds formed with alkoxychlorotitaniums withstood repeated recrystallization. All of the double compounds were extremely hygroscopic. When heated in a sealed capillary, they melted over a wide range of temperature. It should be noted that the structures of these compounds are difficult to understand from the point of view of coordination theory, which would lead us to expect the formation of compounds in which the coordination number of the titanium would be six.

We have made use of the ability of alkoxychlorotitaniums to give stable double compounds with piperidine in order to isolate them in the form of these compounds from the reaction mixtures obtained by treating alkyl orthotitanates with $TiCl_4$. The alkyl orthotitanate, titanium tetrachloride, and piperidine were taken in the proportions required by equations (IV), (V), and (VI), and the double compounds formed by piperidine with a trialkoxychloro-, dialkoxydichloro-, and alkoxytrichloro-titanium, respectively, were obtained.

$$2(RO)_4Ti + TiCl_4 + 3C_5H_{11}N = 4(RO)_3TiCl \cdot C_5H_{11}N, \quad (IV)$$

$$(RO)_4Ti + TiCl_4 + 2C_5H_{11}N = 2(RO)_2TiCl_2 \cdot C_5H_{11}N, \quad (V)$$

$$(RO)_4Ti + 3TiCl_4 + 4C_5H_{11}N = 4ROTiCl_3 \cdot C_5H_{11}N. \quad (VI)$$

We have shown also that reaction between chlorotriethoxytitanium, $TiCl_4$, and piperidine taken in the proportions required by equation (VII) results in the formation of the double compound of piperidine and dichlorodiethoxytitanium:

$$2(RO)_3TiCl + TiCl_4 + 3C_5H_{11}N \rightarrow 3(RO)_2TiCl_2 \cdot C_5H_{11}N \quad (VII)$$

These experiments have shown, first, the wide applicability of this reaction of disproportionation in reverse, and second, that when carried out in a piperidine medium the reaction goes smoothly and gives a good yield of

...double compounds.

When the double compound $(C_2H_5O)_3TiClC_5H_{10}NH$ was treated with ethyl alcohol, a smooth reaction occurred with formation of ethyl orthotitanate and piperidine hydrochloride. In the same way, when the double compounds $(n\text{-}C_3H_7O)_2TiCl_2 \cdot C_5H_{10}NH$ and $(n\text{-}C_4H_9O)_2TiCl_2 \cdot C_5H_{10}NH$ were treated with propyl alcohol and butyl alcohol respectively, chlorotripropoxy- and tributoxychloro-titaniums were formed according to the equations:

$$(n\text{-}C_3H_7O)_2TiCl_2 \cdot C_5H_{10}NH + n\text{-}C_3H_7OH \rightarrow (n\text{-}C_3H_7O)_3TiCl + C_5H_{11}N \cdot HCl.$$

$$(n\text{-}C_4H_9O)_2TiCl_2 \cdot C_5H_{10}NH + n\text{-}C_4H_9OH \rightarrow (n\text{-}C_4H_9O)_3TiCl + C_5H_{11}N \cdot HCl.$$

## EXPERIMENTAL

1. Preparation of $(C_2H_5O)_3TiCl \cdot C_5H_{11}N$

A. From Chlorotriethoxytitanium and Piperidine. Piperidine (2.57 g, i.e. 0.030 mole) was added, with cooling, to 6.30 g (0.024 mole) of chlorotriethoxytitanium, and the mixture solidified. The resulting compound was recrystallized from a mixture of two parts of benzene and one part of petroleum ether. The double compound is readily soluble in chloroform and benzene, but not so readily soluble in petroleum ether.

Found %: C 43.60, 43.28; H 8.77, 8.58; Ti 15.84, 15.85; N 4.91, 4.58.

$(C_2H_5O)_3TiClC_5H_{10}NH$. Calculated %: C 43.43; H 8.63; Ti 15.78; N 4.61.

B. From Ethyl Orthotitanate. A solution of 3.40 g (0.040 mole) of piperidine in 5 ml of benzene was added, with cooling, to 8.1 g (0.030 mole) of ethyl orthotitanate in 15 ml of benzene, and then a solution of 1.89 g (0.01 mole) of $TiCl_4$ in 4 ml of benzene was added dropwise. The double compound crystallized out from the solution. In order to effect more complete precipitation, 20 ml of petroleum ether (b.p. 50-70°) was added to the mixture. The yield of product was 8.6 g (54%); it was recrystallized from a mixture of benzene and petroleum ether.

Found %: C 43.07, 43.27; H 8.82, 8.88; Ti 16.04, 15.18; N 4.55, 4.63.

2. Preparation of $(n\text{-}C_3H_7O)_3TiCl \cdot C_5H_{11}N$ from Chlorotripropoxytitanium

Piperidine (2 ml) was added, with cooling, to a solution of 2.2 g of chlorotripropoxytitanium in 1 ml of petroleum ether. The double compound crystallized out, and it was filtered off and recrystallized from benzene.

Found %: C 48.05, 48.53; H 9.31, 9.12; N 4.22, 4.05.

$(n\text{-}C_3H_7O)_3TiClC_5H_{11}N$. Calculated %: C 48.11; H 9.33; N 4.05.

3. Preparation of $(n\text{-}C_3H_7O)_2TiCl_2 \cdot C_5H_{11}N$ from Propyl Orthotitanate

To a cooled solution of 2.67 g (0.010 mole) of propyl orthotitanate in 3 ml of benzene, first of all a solution of 0.85 g (0.01 mole) of piperidine in 2 ml of benzene was added, and then a solution of 1.9 g (0.01 mole) of $TiCl_4$ in 4 ml of benzene; the solution became dark in color. The reaction mixture was heated at 60° for ten minutes and then cooled. Petroleum ether (5 ml) was added and the precipitate that formed was filtered off. The yield of product was 3.5 g. A completely colorless product was obtained when the precipitate was recrystallized from a mixture of equal volumes of benzene and petroleum ether.

Found %: C 41.25, 41.40; H 7.44, 8.09; N 4.62, 4.51.

$(C_3H_7O)_2TiCl_2C_5H_{11}N$. Calculated %: C 40.99; H 7.82; N 4.34.

4. Preparation of $(C_4H_9O)_3TiCl \cdot C_5H_{11}NH$ from Chlorotriethoxytitanium

To a cooled solution of 2.9 g (0.0092 mole) of chlorotriethoxytitanium in 5 ml of benzene, first of all a solution of 1.39 g (0.0139 mole) of piperidine in 4 ml of benzene was added, and then a solution of 0.96 g (0.0067 mole) of $TiCl_4$ in 3 ml of benzene. The reaction mixture was heated for 30 minutes at 60-65°. The yield of crystalline product which remained when the mixture was cooled was 3.3 g (79%). The double compound was recrystallized from a mixture of benzene and chloroform.

Found %: C 50.79, 50.84; H 7.53, 7.42; N 4.57, 4.69.

$(C_4H_9O)_3TiClC_5H_{10}NH$. Calculated %: C 50.74; H 7.19; N 4.78.

5. Preparation of $(n\text{-}C_4H_9O)_2TiCl_2 \cdot C_5H_{11}N$

A. From Butyl Orthotitanate. To a cooled solution of 3.4 g (0.010 mole) of butyl orthotitanate in 3 ml of benzene, first of all a solution of 1.7 g (0.020 mole) of piperidine in 1 ml of benzene was added, and then a solution of 1.9 g (0.010 mole) of $TiCl_4$ in 3 ml of benzene. The reaction mixture, which had become dark in color, was heated for ten minutes at 50-60°. The mixture was diluted with 10 ml of petroleum ether and then cooled well, and a crystalline precipitate was obtained; the yield was 5 g (85%). The double compound was recrystallized from a mixture of benzene and petroleum ether.

| | | | |
|---|---|---|---|
| | Found %: | Ti 13.63; 13.70; | N 4.05; 4.02 |
| $(C_4H_9O)_2TiCl_2C_5H_{10}NH$. | Calculated %: | Ti 13.68; | N 4.00 |

B. From Tributoxychlorotitanium. The procedure followed that of Expt. No. 4, and 2.7 g of tributoxychlorotitanium, 1.13 g of piperidine, and 0.84 g of $TiCl_4$ in a benzene medium yielded 2 g (57%) of the double salt of piperidine and dibutoxydichlorotitanium. For analysis the product was recrystallized from a mixture of petroleum ether and benzene.

| | | | | |
|---|---|---|---|---|
| | Found %: | C 44.78; 44.60; 44.47; | H 8.55; 8.39; 8.60; | N 4.05; 4.03 |
| $(C_4H_9O)_2TiCl_2C_5H_{11}N$. | Calculated %: | C 44.57; | H 8.35 | N 4.00 |

6. Preparation of $n\text{-}C_3H_7OTiCl_3C_5H_{10}NH$ from Propyl Orthotitanate

To a solution of 1.42 g (0.005 mole) of propyl orthotitanate in 20 ml of a mixture of equal volumes of benzene and petroleum ether first of all a solution of 1.70 g (0.020 mole) of piperidine in 4 ml of benzene was added, and then a solution of 2.84 g (0.015 mole) of $TiCl_4$ in 4 ml of benzene. The reaction mixture turned orange at first, and later became greenish yellow. Petroleum ether (15 ml) was added, and 5.2 g (87%) of precipitate was separated. The product was recrystallized from benzene.

| | | | | |
|---|---|---|---|---|
| | Found %: | C 32.18; 32.46; | H 6.17; 6.23; | Ti 15.79; 15.68; |
| | | N 4.65; 4.71 | | |
| $C_3H_7OTiCl_3C_5H_{10}NH$. | Calculated %: | C 32.16; | H 6.07; | Ti 16.06; |
| | | N 4.69 | | |

7. Preparation of $n\text{-}C_4H_9OTiCl_3C_5H_{10}NH$ from Butyl Orthotitanate

The procedure followed that of the preceding experiment and 1.70 g of butyl orthotitanate, 1.70 g of piperidine, and 2.84 g of $TiCl_4$ yielded 5 g (80%) of the double compound, which was recrystallized from benzene.

| | | | | | |
|---|---|---|---|---|---|
| | Found %: | C 35.11; 34.98; | H 6.45; 6.51; | N 4.46; 4.25; | Cl 34.19; 34.25 |
| $C_4H_9OTiCl_3C_5H_{11}N$ | Calculated %: | C 34.58; | H 6.44; | N 4.48; | Cl 34.07 |

8. Preparation of $CH_2 = CH - CH_2OTiCl_3C_5H_{10}NH$

The procedure was that of the preceding experiments, and 1.44 g of allyl orthotitanate, 1.73 g of piperidine, and 2.90 g of $TiCl_4$ yielded 4.8 g (77%) of the double compound, which was recrystallized from benzene.

| | | | |
|---|---|---|---|
| | Found %: | C 32.73; 32.79; | H 5.60; 5.62 |
| $CH_2 = CHCH_2OTiCl_3 \cdot C_5H_{10}NH$. | Calculated %: | C 32.40; | H 6.48; |

9. Action of Ethyl Alcohol on $(C_2H_5O)_2TiClC_5H_{11}N$

The recrystallized double compound $(C_2H_5O)_2TiClC_5H_{11}N$ (3.5 g) was dissolved in 35 ml of benzene, and to the clear filtered solution 1.4 g of absolute ethyl alcohol was added at room temperature. There was an immediate precipitate of piperidine hydrochloride. The reaction mixture was cooled, and the precipitate was separated, washed with petroleum ether, and dried over $CaCl_2$. The yield of product was 1.3 g (83%); after recrystallization from alcohol it melted at 244-245°. Solvent was driven from the filtrate at the water pump (80°, 40 mm). The residue weighed 3.3 g (74%). The ethyl orthotitanate obtained distilled over at 127-127.5° at 1.5 mm, and had $n_D^{20}$ 1.5105. For ethyl orthotitanate the literature [3] gives b.p. 128-129° (1.5 mm).

10. Action of Propyl Alcohol on $(n\text{-}C_3H_7O)_2TiClC_5H_{11}N$

The procedure of the preceding experiment was followed, and 8.6 g of the double compound $(n\text{-}C_3H_7O)_2TiClC_5H_{11}N$ and 3 ml of absolute propyl alcohol in a benzene medium yielded 4.5 g (65%) of chlorotripropoxytitanium and 3.2 g (93%) of piperidine hydrochloride. The resulting chlorotripropoxytitanium distilled over at 148-149° (5 mm) and was analyzed in the form of its double salt with piperidine (for analytical results see Expt. No. 2).

12. Action of Butyl Alcohol on $(n\text{-}C_4H_9O)_2TiCl_2 \cdot C_5H_{11}N$

The procedure was that of the last two experiments, and 3[illegible] g of the double compound $(n\text{-}C_4H_9O)_2TiCl_2C_5H_{11}N$ and [illegible] ml of absolute butyl alcohol in a benzene medium yielded [illegible].3 g ([illegible]%) of crude tributoxychlorotitanium and [illegible] g [illegible]% of piperidine hydrochloride. The resulting tributoxychlorotitanium distilled over at 165-166° (4 mm). It was converted into the double compound of dibutoxydichlorotitanium, and piperidine which was analyzed (for analytical results see Expt. No. 5B).

## SUMMARY


1. It has been shown that alkyl orthotitanates and trialkoxychloro-, dialkoxydichloro-, alkoxytrichloro-titaniums form crystalline double compounds with piperidine having the composition $(RO)_nTiCl_{4-n} \cdot C_5H_{10}NH$, n = 1, 2, or 3).

2. It has been found that the reaction between alkyl orthotitanates and titanium tetrachloride (the reverse of [illegible] proceeds smoothly in presence of the calculated amount of piperidine with formation of double compounds of piperidine with alkoxychlorotitaniums in high yield.

3. Double compounds of the following compositions have been prepared:

$(C_2H_5O)_3TiCl \cdot C_5H_{10}NH$; $(n\text{-}C_3H_7O)_3TiCl \cdot C_5H_{10}NH$;

$(C_2H_5O)_2TiCl_2 \cdot C_5H_{10}NH$; $(n\text{-}C_3H_7O)_2TiCl_2 \cdot C_5H_{10}NH$;

$(n\text{-}C_4H_9O)_2TiCl_2 \cdot C_5H_{10}NH$; $n\text{-}C_3H_7OTiCl_3 \cdot C_5H_{10}NH$;

$n\text{-}C_4H_9OTiCl_3 \cdot C_5H_{10}NH$; $CH_2=CH-CH_2OTiCl_3 \cdot C_5H_{10}NH$


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# SYNTHESIS OF STEREOISOMERIC ORGANOMERCURY COMPOUNDS VIA ORGANOLITHIUM COMPOUNDS

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In a series of investigations carried out in our laboratory a study has been made of the stereochemistry of metal-exchange reactions given by cis-and trans-2-chlorovinyl organometallic compounds [1-6]. In a paper by two of the present authors it was concluded that in electrophilic and radical exchange reactions of metal attached to an olefin carbon the geometric configuration is retained [7].

It was important to verify the correctness of this conclusion by examining the behavior of organometallic compounds in which an unsaturated purely hydrocarbon radical is attached to metal at the olefin carbon responsible for the geometric isomerism.

Very few such compounds are described in the literature; those described are mainly organomagnesium and organolithium compounds that have not been isolated in the pure state (8-12). Practically nothing is known about alkenyl derivatives of heavy metals [13]. Styrylmercury, styryltin, and styrylthallium derivatives have been prepared by one of us, working with Kudryavtseva but each of them was obtained in only one stereoisomeric form [14]. Hence, in order to carry out the desired investigation it was first necessary to synthesize the cis and trans forms of suitable mercury derivatives of hydrocarbons in which the metal was attached to an unsaturated carbon. The present paper deals with the synthesis of stilbene derivatives of this type. We prepared them by double decomposition between the geometric isomers of 1,2-diphenylvinyllithium [12] and mercuric chloride:

$$C_6H_5CH=CBrC_6H_5 \xrightarrow{C_4H_9Li} C_6H_5CH=CLiC_6H_5 \xrightarrow{HgCl_2} [C_6H_5CH=CC_6H_5]_2Hg.$$

1,2-Diphenylvinyllithium was formed when trans-α-bromostilbene was treated with butyllithium in an ether-benzene medium at a temperature of −30° to −20°. When mercuric chloride was added slowly at the same temperature to the resulting solution of the lithium reagent, a precipitate of bis(1,2-diphenylvinyl)mercury began to form. This compound was found to be of very low solubility in benzene, and practically insoluble in ether, alcohol, chloroform, and acetone. It could be recrystallized from xylene and dioxan and it melted at 243-244°, without decomposition. Yields of 50-60% of bis(1,2-diphenylvinyl)mercury were attained. From the ether-benzene solution obtained after decomposition of the reaction mixture and separation of the insoluble bis(1,2-diphenylvinyl)mercury, it was possible to isolate a very small amount of 1,2-diphenylvinylmercury chloride, and also unchanged trans-α-bromostilbene (30-40% of the amount taken for reaction).

It was shown that raising the reaction temperature lowered the yield of the mercury compound, and that increase in the duration of the reaction had no effect on the yield. In all of the experiments the main product was bis(1,2-diphenylvinyl)mercury, and 1,2-diphenylvinylmercury was obtained as a by-product, irrespective of the molar proportions of reactants and the order of their addition.

1,2-Diphenylvinyllithium was also prepared directly by reaction of trans-α-bromostilbene with lithium in ether at 20-35°. When treated with mercuric chloride, the resulting lithium reagent yielded bis(1,2-diphenylvinyl) mercury (m.p. 243-244°) in 20% yield and 1,2-diphenylvinylmercury chloride in 13% yield.

After being heated for a long time with an alcoholic solution of mercuric chloride, the high-melting bis (1,2-diphenylvinyl)mercury reacted with formation of 1,2-diphenylvinylmercury chloride in almost quantitative yield. This compound melted at 141-142°; it was found to be highly soluble in alcohol and chloroform, and moderately soluble in benzene. It was symmerized when treated with potassium iodide in acetone solution, yielding the original bis(1,2-diphenylvinyl)mercury, m.p. 243-244°.

It was symmerized also when treated with butyllithium. In this reaction no formation of mercury was observed, and it is possible that symmerization by means of butyllithium passes through the stage of an unstable unsymmetrical full organomercury compound:

$$2C_6H_5CH=C(HgCl)C_6H_5 + 2C_4H_9Li \rightarrow [2C_6H_5CH=C(HgC_4H_9)C_6H_5 + 2LiCl] \rightarrow$$

$$\rightarrow [C_6H_5CH=CC_6H_5]_2Hg + (C_4H_9)_2Hg.$$

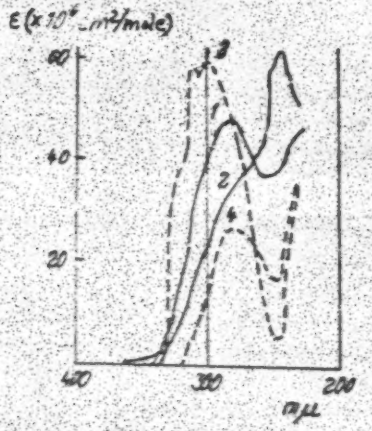
The synthesis of the other stereoisomer of the stilbene mercury derivative was effected by a procedure analo-

ous to that described for the compound of m.p. 243-244°. For this isomer, however, some difficulties were encountered, and it was found that only by the observation of strictly defined conditions during the preparation of the lithium reagent could an organomercury compound stereoisomeric to the above-described bis(1,2-diphenylvinyl) mercury be obtained. Thus, when the reaction between cis-α-bromostilbene and butyllithium was carried out at a temperature not exceeding −40° to −35° and in as short a time as possible, a 50% yield was obtained of a bis(1,2-diphenylvinyl)mercury of m.p. 145-147°, very soluble in benzene and moderately soluble in chloroform and alcohol. If, however, the temperature was raised or the duration of reaction was increased in the reaction between cis-α-bromostilbene and butyllithium, then in the subsequent reaction with mercuric chloride, the bis(1,2-diphenylvinyl)mercury of m.p. 243-244° given by trans-α-bromostilbene was formed as by-product, or even as the main product.

When the bis(1,2-diphenylvinyl)mercury of m.p. 145-147° reacted with an alcoholic solution of mercuric chloride, the product was a 1,2-diphenylvinylmercury chloride of m.p. 130-131°, stereoisomeric with the above-described compound of m.p. 141-142°. The substance of m.p. 130-131° was found to be more soluble in methanol, ethanol, and chloroform than the substance of m.p. 141-142°.

When treated with potassium iodide or butyllithium, the low-melting stereoisomer of 1,2-diphenylvinylmercury chloride was symmetrized, yielding the low-melting bis(1,2-diphenylvinyl)mercury. We thus have four organomercury compounds: the stereoisomeric 1,2-diphenylvinylmercury chlorides, melting at 141-142° and 130-131°, and the stereoisomeric bis(1,2-diphenylvinyl)mercurys, melting at 243-244° and 145-147°.

We have tentatively ascribed the trans configuration to the higher-melting member of each pair, and the cis configuration to the lower-melting member. We based our choice on the following considerations: 1) usually, though not always, the stereoisomer having the higher melting point and lower solubility has the trans configuration, and the lower-melting, more readily soluble isomer has the cis configuration; 2) when heated, the lower-melting bis(1,2-diphenylvinyl)mercury is converted into the higher-melting stereoisomer, and it is known that the thermal isomerization of other substances of similar structure is generally in the direction of cis to trans, cis-α-bromostilbene being converted into the trans isomer [15] and cis-stilbene into trans-stilbene [16] (the low-melting bis(1,2-diphenylvinyl) mercury is isomerized also by ultraviolet radiation, a fact that does not conflict with the assumed configuration, since although trans-cis isomerizations often occur in ultraviolet radiation, cis-trans conversions are also known); 3) confirmation of the assumed configurations was found in observations made* of the ultraviolet absorption spectra of stereoisomeric 1,2-diphenylvinylmercury chlorides (see figure).




Ultraviolet absorption spectra: 1) 1,2-diphenylvinylmercury chloride of m.p. 141-142°; 2) 1,2-diphenylvinylmercury chloride of m.p. 130-131° (c = 0.88 · 10⁻⁴ mole per liter of $CH_3OH$); 3) trans-stilbene; 4) cis-stilbene [18].

Definite geometric configurations have often been ascribed to substances on the basis of differences in the ultraviolet spectra of isomers. There is an empirical rule to the effect that trans isomers absorb more strongly in the ultraviolet than cis isomers [17]. The ultraviolet spectra of the stereoisomeric stilbenes [18, 19] and some of their derivatives [20, 21, 22] have been described in the literature, they are in accord with the above rule. It will be seen from the curves given that 1,2-diphenylvinylmercury chloride of m.p. 141-142° absorbs almost twice as strongly as the isomer of m.p. 130-131° (the first absorption maxima on the curves 1 and 2 in the region of 283-275 mμ).

Moreover, when the substances of m.p. 141-142° and 243-244° obtained from trans-α-bromostilbene are decomposed with dilute hydrochloric acid, trans-stilbene is formed quantitatively, and when the substances of m.p. 130-131° and 145-147° obtained from cis-α-bromostilbene are decomposed under the same conditions, the product is cis-stilbene. These results can be explained in two ways: either the original mercury compound has the same configuration as the stilbene that it yields, or in the reaction

$$C_6H_5CH=C(HgX)C_6H_5 + HCl \longrightarrow C_6H_5CH=CHC_6H_5$$

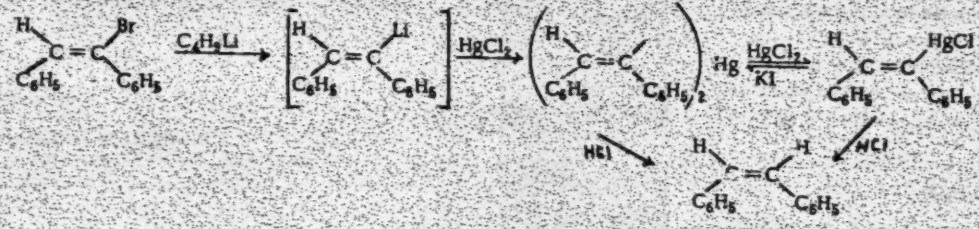
complete reversal of configuration occurs for both isomers. It is more likely that the configuration is retained.

From all these results it may be inferred with a considerable amount of confidence that the substance of m.p. 141-142° is trans-1,2-diphenylvinylmercury chloride, the substance of m.p. 130-131° being its cis isomer, and the

* The absorption spectra were determined for us by T. N. Shkurina at the Optical Laboratory of the Institute of Organic Chemistry.

substance of m.p. 243-244° is trans-bis (1.2-diphenylvinyl)mercury, the substance of m.p. 145-147° being its cis isomer.

Thus, starting from cis- and trans-α-bromostilbenes we have carried out two series of reactions:



(and similarly for the trans isomer).

In all of these reactions the replacement occurs at the olefin carbon responsible for the geometric configuration, and all of these reactions are stereochemically pure, i.e. proceed with retention of the original geometric configuration. In other words, this series of reactions provides confirmation of the rule relating to the retention of geometric configuration in electrophilic and radical exchange reactions [7].

An apparent exception is the reaction in which 1,2-diphenylvinyllithium is formed, for we have shown that by variation in the temperature and duration of reaction during the formation of the lithium reagent, it is possible to obtain trans-bis(1,2-diphenylvinyl)mercury (m.p. 243-244°) from cis-α-bromostilbene. We have succeeded in showing, however, that the change in geometric configuration does not occur at the moment of reaction, but is due to isomerization of the cis-1,2-diphenylvinyllithium. This was proved in a special series of experiments, the results of which are given in Table 1.

TABLE 1

| Expt. No. | Molar ratio of cis bromo cpd. to $C_4H_9Li$ | Temperature of reaction with $C_4H_9Li$ (°C) | Duration of reaction with $C_4H_9Li$ (min) | Molar ratio of cis bromo cpd. to $HgCl_2$ | Temperature of reaction with $HgCl_2$ (°C) | Duration of reaction with $HgCl_2$ (min) | Yield of trans $R_2Hg$ ** (%) | Yield of cis- | |
|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | | $R_2Hg$ (%) | RHgCl (%) |
| 1 | 1:1.25 | (−40) − (−25) | 10 | 2:1 | (−40) − (−25) | 15 | – | 59 | – |
| 2 | 1:1.5 | (−30) − (−15) | 7 | 2:1 | (−40) − (−35) | 30 | 24 | 21 | – |
| 3 | 1:1.25 | (−40) − (−35) | 40 | 2:1 | (−40) − (−35) | 15 | 24 | 22 | – |
| 4 | 1:1.3 | (−30) − (−15) | 60 | 2:1 | (−30) − (−10) | 30 | 70 | – | – |
| 5* | 1:1.5 | (−40) − (−35) | 11 | 2:1 | At first (−40) − (−35), later −15 | 10 | – | 43 | – |
| 6 | 1:1.25 | (−40) − (−35) | 7 | 2:1 | At first (−40) − (−35), later 16−18 | 10 12 hours | – | 31 | – |
| 7 | 1:1.25 | (−20) − (−10) | 30 | 2:1 | 1. (−20) − (−10) 2. (−40) − (−35) | 30 20 | 47 42 | – – | – – |
| 8 | 1:1.25 | (−40) − (−35) ½ reaction mixture | 10 | 1:1 | (−40) − (−35) | 30 | – | – | 40 |
| 9 | 1:1.25 | (−40) − (−35) ½ reaction mixture | 10 | 2:1 | (−40) − (−35) | 20 | – | 51 | – |
| | | At first (−10) − (−35) later (−15) − (−10) | 10 20 | 2:1 | (−30) − (−35) | 20 | 48 | – | – |

* In Expt. No. 5 unchanged cis-α-bromostilbene was isolated.

** R is $C_6H_5CH=CC_6H_5$.

It will be seen from these results that variations in reaction temperature and time for the stage in which the lithium compound is formed have considerable effects on the yields of cis and trans mercury compounds (Expts. 1, 2, 3 and 4). On the other hand, when reaction with mercuric chloride is complete – which requires only a few minutes – neither long standing nor rise in temperature will bring about isomerization of the mercury compound (Expt. No. 5 and 6). Expt. No. 7 (I and II) confirms that isomerization occurs before addition of mercuric chloride, and not during reaction with it. These experiments show that reaction with mercuric chloride is not responsible for the change in geometric configuration.

This conclusion is confirmed also by the fact that the carbonation of cis-1,2-diphenylvinyllithium prepared at different temperatures yielded cis- and trans-2,3-diphenylacrylic acids in varying proportions (Table 2). Since unchanged cis-α-bromostilbene was isolated from the reaction mixture in some experiments (Expt. No. 5, Table 1), it could not be maintained that the original bromo compound had undergone isomerization.

TABLE 2

| Expt. No. | Molar ratio of cis bromo compound to $C_6H_5Li$ | Temperature of reaction with $C_6H_5Li$ (°C) | Duration of reaction with $C_6H_5Li$ (min) | Yield of cis-2,3-diphenylacrylic acid (%) | Yield of trans-2,3-diphenylacrylic acid (%) |
|---|---|---|---|---|---|
| 1 | 1 : 1.25 | (– 40) – (– 35) | 11 | 61 | – |
| 2 | 1 : 1.25 | (– 20) – (– 10) | 11 | 15 | 30 |
| 3 | 1 : 1.25 | (– 20) – (– 10) | 40 | – | 58 |

It now remains to be decided whether the change of configuration occurs in the moment of reaction between butyllithium and cis-α-bromostilbene, or whether it is the cis-1,2-diphenylvinyllithium so prepared that undergoes isomerization.

It may be inferred from the results of Expt. No. 8 that the exchange of bromine for lithium occurs without change of configuration, but that cis-1,2-diphenylvinyllithium is a very unstable substance, which, even at – 40° can exist for only 10-15 minutes, and is isomerized completely at –15°. On account of its low stability, cis-1,2-diphenylvinyllithium cannot be prepared by reaction of cis-α-bromostilbene with lithium, since this reaction requires a temperature of 16-18°.

It is difficult to say whether the isomerization of cis-1,2-diphenylvinyllithium results solely from thermal action or whether there is also some other factor, for we have not obtained the lithium compound in a pure state. Its instability is somewhat unexpected, for the temperature at which cis-trans conversion occurs is 180-200° for stilbene itself [16], 200° for cis-α-bromostilbene [15], and 140-160° for the mercury derivative of cis-stilbene that we have synthesized (m.p. 145-147°). It will be seen from the results given in Table 1 that reaction of cis-1,2-diphenylvinyllithium with mercuric chloride does not always yield the symmetrical mercury compound. Under some conditions the sole product may be cis-1,2-diphenylvinylmercury chloride (Expt. No. 8).

## EXPERIMENTAL

### 1. Preparation of trans-Bis(1,2-diphenylvinyl)mercury

All experiments on the reaction of trans-1,2-diphenylvinyllithium with mercuric chloride were carried out in an apparatus provided with stirrer, condenser, dropping funnel, tube for passage of gas, and thermometer immersed in the reaction mixture. A current of dry pure nitrogen was passed through the apparatus.

a) At a temperature of – 30° to – 20° a titrated solution of butyllithium (0.0125 mole) was added to a solution of 3 g (0.01 mole) of trans-α-bromostilbene in 24 ml of benzene and 36 ml of ether (all solvents were carefully purified and dried). The mixture was stirred for 40 minutes, and 1.5 g (0.005 mole) of mercuric chloride was then added at – 30° to – 20°. The mixture was stirred vigorously for a further 40 minutes, and was then decomposed with 50 ml of 5% hydrochloric acid. The precipitate of trans-bis(1,2-diphenylvinyl)mercury was filtered off, and the layers were separated. The yield of trans-bis(1,2-diphenylvinyl)mercury was 2 g (62%). After two recrystallizations from dioxan the product melted at 243-244° and further recrystallizations did not affect the melting point. A very small amount of trans-1,2-diphenylvinylmercury chloride (m.p. after recrystallization from alcohol 139.5-140.5°) was isolated from the ether-benzene layer after removal of solvent, and at the same time 1 g (33% of the amount taken) of unchanged trans-α-bromostilbene was obtained.

Trans-bis(1,2-diphenylvinyl)mercury is almost insoluble in alcohol, ether, petroleum ether, chloroform, and acetone, is of low solubility in benzene, and is moderately soluble in dioxan and xylene.

Found %: C 59.73; 59.76; H 3.69; 3.96; Hg 35.78; 35.71

$C_{28}H_{22}Hg$ Calculated %: C 60.15; H 3.96; Hg 35.88

2) A solution of 2.5 g (0.01 mole) of trans-α-bromostilbene in 10 ml of ether was added at room temperature to 0.15 g (0.02 mole) of lithium in 35 ml of absolute ether. The dissolution of the lithium required four hours, and toward the end of this period the mixture was heated to the boil. When the whole of the lithium had dissolved, the reaction mixture was cooled to −30° to −20°, and 2.65 g (0.01 mole) of mercuric chloride in 80 ml of ether was added. After 30 minutes the mixture was decomposed with 50 ml of 5% hydrochloric acid, the precipitate was filtered off, and the layers were separated. Recrystallization of the precipitate from dioxan yielded 0.75 g (29%) of trans-bis(1,2-diphenylvinyl)mercury, m.p. 239-241°, and 0.5 g of trans-1,2-diphenylvinylmercury chloride, m.p. 141-142°. A little more trans-1,2-diphenylvinylmercury chloride was obtained from the ether layer after removal of solvent (total yield about 13%).

## 2. Reaction of trans-Bis(1,2-diphenylvinyl)mercury with Mercuric Chloride

A mixture of 1.45 g of trans-bis(1,2-diphenylvinyl)mercury, 0.8 g of mercuric chloride, and 25 ml of absolute alcohol was heated for 5 hours 30 minutes in a sealed tube in a boiling water bath. The tube was then opened, and the crystals present were filtered off. The product was 2.05 g (93%) of trans-1,2-diphenylvinylmercury chloride, m.p. 137-139°. One recrystallization from alcohol raised the melting point to 141.5-142°, but further recrystallizations did not raise it beyond this value.

This substance is readily soluble in alcohol, chloroform, and dioxan, moderately soluble in benzene, somewhat soluble in ether, and insoluble in petroleum ether.

Found %: C 40.31; 40.48; H 2.83; 2.71; Hg 48.15

$C_{14}H_{11}ClHg$ Calculated %: C 40.48; H 2.67; Hg 48.30

## 3. Decomposition of trans-Bis(1,2-diphenylvinyl)mercury and of trans-1,2-Diphenylvinylmercury Chloride with Hydrochloric Acid

1) A mixture of 1 g of trans-bis(1,2-diphenylvinyl)mercury and 30 ml of hydrochloric acid (1 : 1) was refluxed for one hour. The reaction mixture was then extracted with ether, and the ether was removed from the extract. The product was 0.6 g (95%) of trans-stilbene, m.p. 123-124° after a single recrystallization from alcohol. There was no depression in a mixture test with an authentic sample.

2) Trans-1,2-Diphenylvinylmercury chloride (3 g) was decomposed with 50 ml of HCl (1 : 1) under the same conditions. The product was 1.25 g (96%) of trans-stilbene, m.p. 122-123.5°.

## 4. Symmetrization of trans-1,2-Diphenylvinylmercury Chloride

1) Symmetrization with Potassium Iodide. A solution of 4 g (0.024 mole) of potassium iodide in 62 ml of acetone and 7 ml of water was added to a solution of 1 g (0.0024 mole) of trans-1,2-diphenylvinylmercury chloride in a mixture of 50 ml of acetone and 5 ml of water. A precipitate of fine needles began to form immediately. The mixture was set aside for one day at room temperature, and the precipitate was then filtered off. The product was 0.55 g (85%) of trans-bis(1,2-diphenylvinyl)mercury, which melted at 243-244° after one recrystallization from dioxan and showed no depression in a mixture melting test with the trans-bis(1,2-diphenylvinyl)mercury obtained from the lithium reagent.

2) Symmetrization with Butyllithium. A solution of 1 g of trans-1,2-diphenylvinylmercury chloride in a mixture of 40 ml of benzene and 60 ml of ether was cooled to −40° to −30°, and, in an atmosphere of nitrogen, an equimolecular amount of a titrated ethereal solution of butyllithium was added. A precipitate began to appear immediately. The mixture was allowed to stand at the same temperature for 40 minutes, and was then decomposed with 50 ml of 3% hydrochloric acid. The precipitate of trans-bis(1,2-diphenylvinyl)mercury was filtered off, and the layers were separated. The yield of trans-bis(1,2-diphenylvinyl)mercury was 0.5 g (83%). It melted at 239-241° and showed no melting point depression in admixture with the sample obtained with the aid of the lithium reagent. A very small amount of trans-1,2-diphenylvinylmercury chloride, m.p. 139-141°, was isolated from the ether-benzene layer.

## 5. Preparation of cis-Bis(1,2-diphenylvinyl)mercury

The preparation of cis-bis(1,2-diphenylvinyl)mercury was carried out in the apparatus used for the preparation of the trans isomer. A titrated ethereal solution of butyllithium (0.025 mole) was added at −40° to −35° to a solution of 5 g (0.02 mole) of cis-α-bromostilbene in a mixture of 40 ml of benzene and 60 ml of ether. Care was taken that the temperature did not exceed −35°. After a period of ten minutes from the beginning of the addition

of butyllithium, 2.55 g (0.01 mole) of mercuric chloride in 200 ml of ether was added to the solution of lithium reagent, the temperature being constantly maintained at −40° to −35°. The reaction with mercuric chloride was complete in 10-15 minutes, its completion being marked by the disappearance of the dark color characteristic of the lithium reagent. A completely clear light-yellow solution was obtained. It should be noted that the lithium chloride formed in the reaction was not precipitated; it probably formed a soluble complex. The reaction mixture was decomposed with 50 ml of 3% hydrochloric acid and the layers were separated. The ether-benzene layer, after removal of solvent, yielded 2.7 g (50%) of cis-bis(1-2 diphenylvinyl)mercury, m.p. 145-147° after two recrystallizations from a mixture of benzene and alcohol. Further recrystallizations did not affect the melting point.

cis-Bis(1,2-diphenylvinyl)mercury is highly soluble in benzene and moderately soluble in alcohol and chloroform. A mixture with trans-bis(1,2-diphenylvinyl)mercury melted over the range 140-220°.

| | | | | | |
|---|---|---|---|---|---|
| | | Found % | C 59.80; 59.92; | H 4.18; 4.05; | Hg 35.69 |
| $C_{28}H_{22}Hg$. | | Calculated % | C 60.15; | H 3.96; | Hg 35.88 |

6. Preparation of cis-1,2-Diphenylvinylmercury Chloride

cis-α-Bromostilbene (5 g, i.e. 0.02 mole) was caused to react with butyllithium (0.025 mole) under the conditions described for the preceding experiment. Mercuric chloride (5.2 g, i.e. 0.02 mole) was then added, without solvent, to the reaction mixture. Reaction was allowed to proceed for 30 minutes, and the mixture was then treated as in the preceding experiment. A small amount (14%) of trans-bis(1,2-diphenylvinyl)mercury, m.p. 240-241°, was obtained, and the main product was 3.1 g (40%) of cis-1,2-diphenylvinylmercury chloride, m.p. 130-131° after two recrystallizations from alcohol. Further recrystallizations did not affect the melting point.

cis-1,2-Diphenylvinylmercury chloride is readily soluble in alcohol and chloroform, but somewhat less soluble in benzene.

| | | | | | |
|---|---|---|---|---|---|
| | | Found % | C 40.28; 40.44 | H 2.71; 2.77; | Hg 48.42; 48.40 |
| $C_{14}H_{11}ClHg$. | | Calculated % | C 40.48; | H 2.67 | Hg 48.30 |

7. Decomposition of cis-Bis(1,2-diphenylvinyl)mercury and of cis-1,2-Diphenylvinylmercury Chloride with Hydrochloric Acid.

1) A mixture of 2 g of cis-bis(1,2-diphenylvinyl)mercury and 40 ml of HCl (1 : 1) was heated for 30 minutes, and was then extracted with ether. The oily liquid remaining after removal of ether was heated for 40 minutes at 180-200°. The product was 1.2 g (92%) of trans-stilbene, m.p. 123-124° after one recrystallization from alcohol. The melting point was undepressed by admixture of authentic material.

2) cis-1,2-Diphenylvinylmercury chloride (3 g) was decomposed with 50 ml of HCl under the same conditions, and yielded a noncrystallizing oil of cis-stilbene, which was isomerized to the trans isomer as described above. The product was 1.25 g (96%) of trans-stilbene, m.p. 122-123°, undepressed by admixture of authentic material.

8. Reaction of cis-α-Bromostilbene with Lithium

The reaction of cis-α-bromostilbene with lithium was carried out under the conditions used for the trans isomer, but the reaction temperature was lowered to 16-18°. The products obtained from 5 g of cis-α-bromostilbene were 0.8 g (10%) of trans-bis(1,2-diphenylvinyl)mercury, m.p. 242-244°, and 1.3 g (25%) of trans-1,2-diphenylvinylmercury chloride, m.p. 141-141.5°.

9. Carbonation of cis-1,2-Diphenylvinyllithium

cis-1,2-Diphenylvinyllithium, prepared under various temperature conditions, was subjected to carbonation with solid carbon dioxide. The reaction mixture was decomposed with 3% hydrochloric acid and extracted with benzene. Aniline was added to the dried benzene solution, and trans-2,3-diphenylacrylic acid was precipitated as its anilinic salt, m.p. 127-128° (the literature [12] gives 128°). The filtrate was treated with 15% aqueous caustic potash, and acidification of the solution yielded cis-2,3-diphenylacrylic acid, m.p. 172-173° (the literature [12] gives 173-174°). The experimental results are given in Table 2.

10. Symmetrization of cis-1,2-Diphenylvinylmercury Chloride

1) Symmetrization with Potassium Iodide. A solution of 4 g (0.024 mole) of potassium iodide in a mixture of 50 ml of acetone and 7 ml of water was added to a solution of 1 g (0.0024 mole) of cis-1,2-diphenylvinylmercury chloride in 50 ml of acetone. The mixture stood at room temperature for two days. The small amount of inorganic precipitate was filtered off, and some of the acetone was driven off the filtrate under reduced pressure. When the solution was cooled, crystals appeared, and 0.35 g (52%) of cis-bis(1,2-diphenylvinyl)mercury was obtained; it melted

at 145-147° after recrystallization from a mixture of alcohol and chloroform, and the melting point was not depressed by admixture of material prepared from cis-1,2-diphenylvinyllithium. The residue remaining after complete removal of acetone was treated with boiling benzene and, as a result, 0.2 g of the original cis-1,2-diphenylvinylmercury chloride, m.p. 130-131°, was isolated.

2) Symmetrization with Butyllithium. A solution of 1 g of cis-1,2-diphenylvinylmercury chloride in a mixture of 40 ml of benzene and 60 ml of ether was cooled to −40° to −30°, and, at this temperature in an atmosphere of nitrogen, an equimolecular amount of a titrated ethereal solution of butyllithium was added. The mixture, which remained completely clear, was allowed to stand at −40° to −30° for 40 minutes. It was then decomposed with 50 ml of 5% hydrochloric acid, the layers were separated, and the ether-benzene layer was dried with calcium chloride. The solvent was removed under reduced pressure, and the residue yielded 0.4 g (66%) of cis-bis(1,2-diphenylvinyl)-mercury, m.p. 145-147° after one recrystallization from a mixtute of alcohol and benzene. A mixture test with a sample prepared via the lithium reagent showed no depression.

## 11. Reaction of cis-Bis(1,2-diphenylvinyl)mercury with Mercuric Chloride

A mixture of 1 g of cis-bis(1,2-diphenylvinyl)mercury, 0.5 g of mercuric chloride, and 40 ml of absolute alcohol was heated in a sealed tube for five hours in a boiling water bath. The tube was then opened, and the crystals that had formed were filtered off. The product was 1.1 g (79%) of cis-1,2-diphenylvinylmercury chloride, m.p. 130-131° after recrystallization from alcohol. A mixture test with a sample prepared via cis-1,2-diphenylvinyllithium showd no depression. After removal of solvent about 0.1 g of unchanged cis-bis(1,2-diphenylvinyl)mercury was isolated.

## 12. Ultraviolet Irradiation of cis-Bis(1,2-diphenylvinyl)mercury

A solution of 1 g of cis-bis(1,2-diphenylvinyl)mercury in 50 ml of chloroform was exposed to the radiation from a PRK-4 quartz lamp for three hours. Already after 30 minutes a precipitate of fine needles began to appear, and this precipitate had become appreciable by the end of the three hours, when it was filtered off. The product was 0.50 g (50%) of trans-bis(1,2-diphenylvinyl)mercury, and without recrystallization it melted at 243-244°, undepressed by admixture of an authentic sample. After removal of chloroform, 0.3 g (30% of the amount taken) of unchanged cis-bis-(1,2-diphenylvinyl)mercury was separated. A slight deposit of univalent mercury salt formed on the walls of the flask.

It was not found possible to convert trans isomers of mercury derivatives of stilbene into their cis isomers. Prolonged ultraviolet irradiation destroyed the substances investigated, but did not convert them into cis modifications.

## 13. Thermal Isomerization of cis-Bis(1,2-diphenylvinyl)mercury

cis-Bis(1,2-diphenylvinyl)mercury (0.5 g) was heated at 140-160° in a sealed tube for four hours. In the course of this treatment mercury separated at the bottom of the tube. After the heating the contents of the tube were treated successively with benzene and dioxan. From the dioxan 0.25 g (50%) of trans-bis(1,2-diphenylvinyl)mercury, m.p. 242-244°, was separated; it showed no depression in a mixture test with an authentic sample. From the benzene 0.1 g of trans-stilbene, m.p. 121-122°, was separated, and its melting point was not depressed by admixture of authentic stilbene.

## SUMMARY

1. By treatment of the geometric isomers of 1,2-diphenylvinyllithium with mercuric chloride, the stereoisomeric bis(1,2-diphenylvinyl)mercurys have been prepared.

2. By the disymmetrization of the stereoisomeric bis(1,2-diphenylvinyl)mercurys, the stereoisomeric 1,2-diphenylvinyl mercury chlorides have been prepared.

3. An investigation has been made of the symmetrization of the stereoisomeric 1,2-diphenylvinylmercury chlorides with formation of the original bis(1,2-diphenylvinyl)mercurys.

4. A study has been made of the conditions required for the isomerization of cis-1,2-diphenylvinyllithium and of cis-bis(1,2-diphenylvinyl)mercury into the corresponding trans isomers.

5. It has been shown that the investigated exchange reactions occurring at the olefin carbon responsible for geometric isomerism are stereochemically pure and occur without change in the original configuration.

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# ALKYLATION AND ACYLATION OF (CHLOROMERCURI)ACETALDEHYDE

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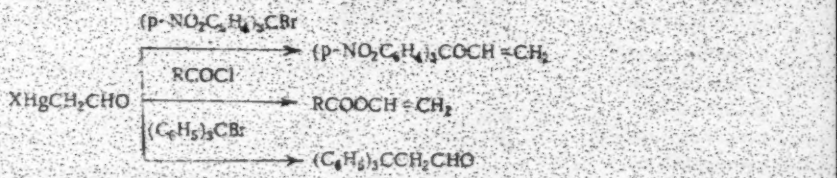
One of the present authors and Lutsenko have already pointed out the dual reactivity of α-mercurated aldehydes and ketones [1, 2, 3]. Thus, when (chloromercuri)acetaldehyde, (chloromercuri)acetone, and 2-(chloromercuri)acetophenone react with chlorotriphenylmethane, the respective products are triphenylmethyl derivatives of acetaldehyde, acetone, and acetophenone; i.e. C-alkylation occurs. When these mercury carbonyl compounds react with acetyl chloride and benzoyl chloride, however, the corresponding vinyl esters of acetic and benzoic acids are formed; i.e. O-alkylation occurs [2]. Further study of the way in which the direction of the reaction (reaction at C or at O) depends on the structure of the alkylating or acylating reagent demands examination of the behavior of a larger number of reagents.

We now describe a study of the reactions of mercurated acetaldehyde with bromotriphenylmethane, with bromotris(p-nitrophenyl)methane, with p-nitrobenzoyl chloride, with chloroacetyl chloride, with trichloroacetyl chloride, with triphenylacetyl chloride, and with phthalimidoacetyl chloride. All of the acid chlorides investigated, irrespective of their structure, reacted with (chloromercuri)acetaldehyde with formation of the corresponding vinyl esters in 40-58% yield. The structures of the resulting vinyl esters, which, apart from vinyl chloroacetate, have not been described in the literature, were established by acid hydrolysis. Acetaldehyde was identified as its p-nitrophenylhydrazone, and the acids were identified by their melting points; the phenacyl derivatives of chloroacetic and trichloroacetic acids were prepared.

Bromotriphenylmethane behaved like chlorotriphenylmethane [2] in its reaction with (bromomercuri)acetaldehyde, triphenylmethyl-substituted acetaldehyde (3,3,3-triphenylpropionaldehyde) being formed; no triphenylmethyl vinyl ether was formed. The identity of the 3,3,3-triphenylpropionaldehyde was proved by preparing its p-nitrophenylhydrazone, and by the absence of depression in a mixture melting test with the 3,3,3-triphenylpropionaldehyde prepared by the ozonization of 4,4,4-triphenyl-1-butene, which was prepared from chlorotriphenylmethane and allyl chloride.

Bromotris(p-nitrophenyl)methane behaved like the acid chlorides in its reaction with (bromomercuri acetaldehyde. This reaction provides a convenient method for the synthesis of the vinyl ether of tris(p-nitrophenyl)methanol, which has not been described previously.




The structure of the vinyl ether of tris(p-nitrophenyl)methanol was proved by its addition reaction with bromine, the absence of reactions for aldehydes, and the formation of tris(p-nitrophenyl)methanol by acid hydrolysis.

Alkyl halides, including even such compounds as allyl chloride and benzyl chloride, did not react with mercurated acetaldehyde. The alkylation reaction was given only by bromotriphenylmethane (which reacted like chlorotriphenylmethane [2], which yielded 3,3,3-triphenylpropionaldehyde. Intensification of the electrophilic character of the reagent by the introduction of three nitro groups [bromotris(p-nitrophenyl)methane] led to a change in the direction of the reaction. Bromotris(p-nitrophenyl)methane reacted like the acid chlorides and gave a vinyl ether. Picryl chloride did not react with mercurated acetaldehyde. Owing to the selective reactivity of mercurated acetaldehyde toward halogen compounds, the choice of alkylating reagents is limited.

Thus, in all of the examples studied of the acylation of mercurated acetaldehyde, reaction is at the oxygen atom, i.e. occurs with transfer of the reaction center along the conjugated system of Hg–C and C=O bonds, whereas alkylation, depending on the reagent, may occur either with or without transfer of reaction center.

## EXPERIMENTAL

### Reaction of (Bromomercuri)acetaldehyde with Bromotriphenylmethane

A solution of 3 g of bromotriphenylmethane in 25 ml of absolute benzene was added to 3 g of dry, carefully

ground (bromomercuri)acetaldehyde that had not been recrystallized. The mixture was heated for two hours at 50-60° and for two hours at the boil. The precipitate was then filtered off, and the benzene was distilled off. The product was 2.4 g of crude 3,3,3-triphenylpropionaldehyde melting at 85-95°, and 2.0 g of this was recrystallized several times, first from ligroin, and then from methanol. The 3,3,3-triphenylpropionaldehyde so obtained (0.9 g) melted at 99-100.5°, and there was no depression in a mixture test with 3,3,3-triphenylpropionaldehyde obtained by the ozonization of 4,4,4-triphenyl-1-butene (mixture melted at 99-100.5°). The p-nitrophenylhydrazone of 3,3,3-triphenylpropionaldehyde, m.p. 245-246°, was recrystallized from toluene.

| | | |
|---|---|---|
| | Found % | N 10.25; 10.17 |
| $C_{27}H_{23}N_3O_2$. | Calculated % | N 9.97 |

To a solution of 0.3 g of crude 3,3,3-triphenylpropionaldehyde in 1 ml of chloroform, 2 ml of a chloroform solution of 0.028 g of bromine was added. The color of the solution, as judged by comparison with a standard color, did not change over a period of five minutes. Hence, no triphenylmethyl vinyl ether was formed in the reaction of bromotriphenylmethane with mercurated acetaldehyde.

Preparation of 4,4,4-Triphenyl-1-butene(allyltriphenylmethane). A solution of 3 g of allyl chloride in 100 ml of absolute ether was added gradually with vigorous mechanical stirring to 10 g of magnesium that had been activated with iodine, and to the mixture so obtained a solution of 17 g of chlorotriphenylmethane and 10 g of allyl chloride in 250 ml of absolute ether was added slowly. The reaction mixture was heated with constant stirring for six hours, and was then decomposed with dilute hydrochloric acid. The product was 12 g (70%) of 4,4,4-triphenyl-1-butene, m.p. 70.5-71° (recrystallized from methanol).

| | | |
|---|---|---|
| | Found % | C 92.91; 92.79; H 7.15; 7.15 |
| $C_{22}H_{20}$. | Calculated % | C 92.91; H 7.09; |

Ozonization of 4,4,4-Triphenyl-1-butene. Ozonized oxygen (0.042 g of ozone per liter) was passed for ten hours through a solution of 7 g of 4,4,4-triphenyl-1-butene in 50 ml of chloroform. The chloroform was driven off under reduced pressure at 26°, and the oil that remained was treated with water, first in the cold, and then with heating. It was then dissolved in ether, and the solution was washed with water, with 5% caustic soda solution, and again with water. It was dried with sodium sulfate, and the ether was driven off. The residue crystallized out when petroleum ether was added. Two recrystallizations (from petroleum ether and from methanol) yielded 3 g of 3,3,3-triphenylpropionaldehyde, m.p. 98.5-100°. The yield was 43%.

| | | |
|---|---|---|
| | Found % | C 87.96; 88.13; H 6.44; 6.28 |
| $C_{21}H_{18}O$. | Calculated % | C 88.08; H 6.33; |

Hellerman and Garner [4] give m.p. 101°.

Reaction of (Bromomercuri)acetaldehyde with Bromotris(p-nitrophenyl)methane

A solution of 3.8 g of bromotris(p-nitrophenyl)methane in 80 ml of dry chloroform was mixed with 3.8 g of carefully ground (bromomercuri)acetaldehyde, and the mixture was set aside for two days and then heated for three hours in a water bath. The chloroform solution was filtered from the precipitate, washed several times with a 10% solution of sodium carbonate and with water, and dried with sodium sulfate, the chloroform was distilled off. Recrystallization from acetone yielded 1.4 g (40%) of tris(p-nitrophenyl)methyl vinyl ether, m.p. 164-164.5° (with decomposition).

| | | |
|---|---|---|
| | Found % | C 60.12; 60.25; H 3.61; 3.74 |
| $C_{21}H_{13}N_3O_7$ | Calculated % | C 59.85; H 3.58 |

Tris(p-nitrophenyl)methyl vinyl ether decolorizes a chloroform solution of bromine and does not react with hydroxylamine and p-nitrophenylhydrazine. It is hydrolyzed by hydrochloric acid with formation of tris(p-nitrophenyl)methanol.

Bromotris(p-nitrophenyl)methane was prepared by heating 6 g of tris(p-nitrophenyl)methane with 4 g of dry bromine at 160-170° in a sealed tube for ten hours. The excess of bromine was absorbed by caustic alkali in a vacuum desiccator, and the bromotris(p-nitrophenyl)methane was then washed with ether and boiled with a small amount of benzene to remove residual bromine. The yield was 5.9 g (82%), m.p. 188-190°.

Data in the literature: Ziegler and Boye [6], decomposition temperature 191°; Lewis, Lipkin, and Magel [6], m.p. 185.9-186.5°; Leffler [7], m.p. 200-200.5°.

Hydrolysis of Tris(p-nitrophenyl)methyl Vinyl Ether. A chloroform solution of 0.2 g of tris(p-nitrophenyl)methyl vinyl ether was heated for 30 minutes with 10 ml of concentrated hydrochloric acid. The product was 0.06 g (84%) of tris(p-nitrophenyl)methanol, which melted at 188-190° after several recrystallizations from benzene. A mixture melting test with authentic tris(p-nitrophenyl)methanol gave no depression (m.p. 189-191°).

## Reaction of (Chloromercuri)acetaldehyde with Chloroacetyl Chloride

A solution of 19 g of chloroacetyl chloride in 15 ml of benzene was added to a suspension of 50 g of dry, carefully ground, crude (not recrystallized*) (chloromercuri)acetaldehyde in 45 ml of absolute benzene. The mixture was shaken until no further rise in temperature occurred; and it was then heated at 60-70° for two hours and at the boil for two hours. The precipitate was filtered off and washed with benzene, and excess of benzene was driven off. Two distillations through a 28-cm Burpé fractionating column yielded 10.6 g (58%) of vinyl chloroacetate, b.p. 134.5-135.5° (771 mm); 62-63.5° (58 mm); $n_D^{20}$ 1.4460; $d_4^{20}$ 1.1941; MR 26.89; $C_4H_5O_2ClF$. Calculated MR 26.73.

| | | | |
|---|---|---|---|
| | Found %: | C 39.95; 40.02; | H 4.33; 4.27 |
| $C_4H_5O_2Cl$. | Calculated %: | C 39.91 | H 4.09 |

Wiley [8] gives b.p. 37-38° (16 mm); $n_D^{25}$ 1.4422.

The solid residue from the distillation was extracted with benzene, and the benzene was distilled off. Chloroacetic acid, m.p. 56-57°, was obtained; there was no depression in a mixture test (57-59°).

Hydrolysis of Vinyl Chloroacetate. A mixture of 0.64 g of vinyl chloroacetate and 25 ml of 20% sulfuric acid was boiled for 30 minutes. The acetaldehyde evolved was trapped in a solution of 0.81 g of p-nitrophenylhydrazine in 100 ml of 15% acetic acid, and 0.8 g (80%) of acetaldehyde p-nitrophenylhydrazone was obtained. After recrystallization from 50% alcohol it melted at 123-125°, and there was no depression in a mixture test (124-125°).

The aqueous solution of sulfuric and chloroacetic acids that remained in the flask after removal of acetaldehyde was neutralized with caustic soda. The solution was then rendered acid to litmus by addition of one drop of sulfuric acid, and a solution of 0.5 g of 2-bromoacetophenone in 10 ml of alcohol was added. The mixture was refluxed for one hour, and 0.25 g (47%) of phenacyl chloroacetate was obtained, melting at 94-95° after recrystallization from alcohol. A mixture with the phenacyl ester obtained from pure chloroacetic acid (m.p. 96°) melted without depression (95-96°).

## Reaction of (Chloromercuri)acetaldehyde with Trichloroacetyl Chloride

The procedure was that described for chloroacetyl chloride. 46 g of (chloromercuri)acetaldehyde and 27 g of trichloroacetyl chloride yielded 14 g (53%) of vinyl trichloroacetate, b.p. 67-68° (42 mm); $n_D^{20}$ 1.4670; $d_4^{20}$ 1.4147; $MR_D$ 37.24; $C_4H_3O_2Cl_3F$. Calculated MR 36.46.

| | | | |
|---|---|---|---|
| | Found %: | C 25.48; 25.31; | H 1.74; 1.72 |
| $C_4H_3O_2Cl_3$. | Calculated %: | C 25.36; | H 1.61 |

Hydrolysis of Vinyl Trichloroacetate. The procedure was that described for vinyl chloroacetate. The yield of acetaldehyde p-nitrophenylhydrazone was 73%, and that of phenacyl trichloroacetate (m.p. 49-50°) was 52%. Mixture tests were undepressed.

## Reaction of (Chloromercuri)acetaldehyde with Phenylacetyl Chloride

The procedure was that described for chloroacetyl chloride. 44 g of (chloromercuri)acetaldehyde and 22 g of phenylacetyl chloride yielded 14.2 g (50%) of vinyl phenylacetate, b.p. 80-81° (2 mm); $n_D^{20}$ 1.5163; $d_4^{20}$ 1.0533; MR 46.51. $C_{10}H_{10}O_2F_4$. Calculated %: MR 45.97.

| | | | |
|---|---|---|---|
| | Found %: | C 74.07; 74.00; | H 6.44 6.42 |
| $C_{10}H_{10}O_2$. | Calculated %: | C 74.05; | H 6.22 |

Hydrolysis of Vinyl Phenylacetate. The procedure was that described for vinyl chloroacetate. 1.8 g of the ester being boiled with 20% sulfuric acid for 1 hour 30 minutes. The yield of acetaldehyde p-nitrophenylhydrazone, m.p. 124-126°, was 1.4 g (67%), and a mixture test was not depressed (124-126°). The yield of phenylacetic acid, m.p. 72-74°, was 1.2 g (89%), and again a mixture test was not depressed (73-75°).

## Reaction of (Chloromercuri)acetaldehyde with Triphenylacetyl Chloride

The procedure was that described for chloroacetyl chloride. The benzene was distilled off, and the residue was treated with ligroin, the insoluble part being filtered off and recrystallized several times from alcohol. It was then dissolved in hot benzene and precipitated with petroleum ether. A yield of 0.5 g (48%) of vinyl triphenylacetate, m.p. 126.5-127.5°, was obtained from 0.9 g of triphenylacetyl chloride and 1 g of (chloromercuri)acetaldehyde.

* The reaction goes better with (chloromercuri)acetaldehyde that has not been recrystallized.

Found %: C 84.05; 84.16; H 5.83; 5.95

$C_{22}H_{18}O_2$. Calculated %: C 84.05; H 5.76

Vinyl triphenylacetate is readily soluble in benzene, chloroform, hot alcohol, and hot ligroin. It is stable in the air.

Hydrolysis of Vinyl Triphenylacetate. The vinyl ester (0.8 g) was boiled for one hour with a mixture of 5 ml of 35% sulfuric acid, 5 ml of water, and 10 ml of dioxan. The yield of acetaldehyde p-nitrophenylhydrazone was 0.12 g (42%). The residue in the flask was poured into 100 ml of cold water. The precipitate was filtered off and treated with 120 ml of a hot 10% solution of caustic potash. The insoluble part (0.3 g) - which was vinyl triphenylacetate, since a mixture test with the original substance showed no depression - was filtered off. The yield of triphenylacetic acid was 0.4 g (87% on the amount of ester that reacted). After recrystallization from alcohol it melted at 263-265°, and a mixture test was undepressed.

Reaction of (Chloromercuri)acetaldehyde with p-Nitrobenzoyl Chloride *

The procedure was that described for chloroacetyl chloride. The benzene solution was washed with 5% caustic soda solution and with water, and was dried with sodium sulfate. The benzene was distilled off, and the residue was recrystallized from alcohol. A yield of 4.3 g (55%) of vinyl p-nitrobenzoate, m.p. 69.5-70.5°, was obtained from 7.5 g of p-nitrobenzoyl chloride and 12.5 g of (chloromercuri)acetaldehyde.

Found %: C 55.79; 55.90; H 4.02; 4.07; N 7.53; 7.61

$C_9H_7NO_4$. Calculated %: C 55.86; H 3.66; N 7.26

Hydrolysis of Vinyl p-Nitrobenzoate. The procedure was that described for vinyl chloroacetate, and 0.35 g of the vinyl ester yielded 0.26 g (81%) of acetaldehyde p-nitrophenylhydrazone and 0.18 g (60%) of p-nitrobenzoic acid, m.p. 235-236°. Mixture tests were undepressed.

Reaction of (Chloromercuri)acetaldehyde with Phthalimidoacetyl Chloride *

The procedure was that described for chloroacetyl chloride: 2 g of phthalimidoacetyl chloride and 2.75 g of (chloromercuri)acetaldehyde yielded 0.8 g (40%) of vinyl phthalimidoacetate, m.p. 104-105° after recrystallization from ligroin.

Found %: 62.51; 62.55; H 3.89; 4.07; N 5.86; 5.87

$C_{12}H_9NO_4$. Calculated %: 62.34; H 3.90; N 6.06

Hydrolysis of Vinyl Phthalimidoacetate. The procedure was that described for vinyl chloroacetate: 0.45 g of the vinyl ester yielded 0.2 g (57%) of phthalimidoacetic acid, m.p. 192° after recrystallization from water. A mixture test was not depressed.

## SUMMARY


1. It has been shown that the reaction of mercurated acetaldehyde with carboxylic acid chlorides results in the formation of the corresponding vinyl esters. In a similar way, bromotris(p-nitrophenyl)methane yields the corresponding vinyl ether. In these reactions transfer of reaction center along the system of conjugated Hg–C and C=O bonds occurs.

2. It has been shown that the reaction of mercurated acetaldehyde with bromotriphenylmethane results in the formation of 3,3,3-triphenylpropionaldehyde, i.e. C-alkylation occurs, without transfer of reaction center.

3. The previously undescribed vinyl esters of trichloroacetic, phenylacetic, triphenylacetic, phthalimidoacetic, p-nitrobenzoic acids have been prepared.

4. The synthesis and ozonization of 4,4,4-triphenyl-1-butene have been described.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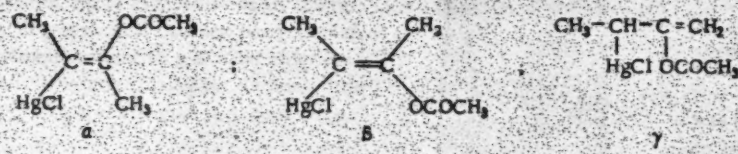
# INVESTIGATION OF THE PRODUCTS OF THE ADDITION OF MERCURY SALTS TO DISUBSTITUTED ACETYLENES

A. E. Borisov, V. D. Vilchevskaya, and A. N. Nesmeyanov

In a previous paper we have described the addition of mercury salts to dimethyl- and diphenyl-acetylenes [1]. These reactions led to the preparation of new organomercury compounds of the ethylene series. Reaction of 2-butyne (dimethylacetylene) with mercuric acetate yielded three isomeric products, the α-, β-, and γ-isomers melting at 140°, 95°, and 130° respectively. The structures of these isomers were proved by ozonization, and it was shown that the α-, and β- compounds formed a pair of geometric isomers, and the γ-compound was structurally isomeric with these:



α β γ

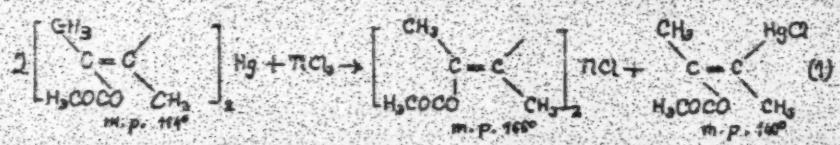
In the same paper we described some of the chemical and physical properties of these compounds.

We now describe a further investigation of the chemical and physical properties of these three compounds. A study of the infrared absorption spectra* has enabled us to determine the geometric configurations of the α- and β-isomers. The absorption spectrum of the α-isomer (Fig. 1) contains a frequency of 1667 $cm^{-1}$ in the characteristic region of the C=C bond, whereas the spectrum of the β-isomer (Fig. 2) contains a frequency of 1655 $cm^{-1}$ in the same region. The spectra contain also a frequency of 1755 $cm^{-1}$ corresponding to the C=O group, which is present in both compounds.

Hence, a higher C=C frequency was found for the α-isomer than that found in the same region for the β-isomer. The more highly symmetrical trans compound generally has the higher C=C frequency [2] and for this reason we have ascribed the trans configuration to the α-isomer, and the cis configuration to the β-isomer. This assignment of configurations is in accord with the fact that the α-isomer is of lower solubility in organic solvents and has a higher melting point than the β-isomer - most trans compounds are related in this way to their cis isomers.

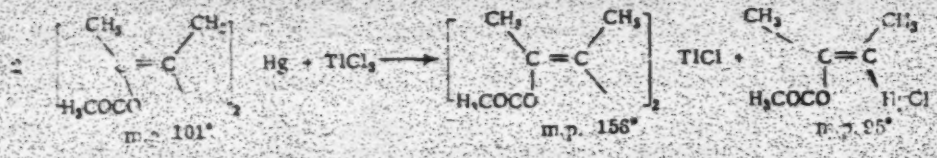
By the same method we have established the configurations of the symmetrical stereoisomers of bis(2-acetoxy-1-methylpropenyl)mercury. The stereoisomer prepared from the α-isomers had a C=C frequency of 1621 $cm^{-1}$ (Fig. 3), whereas its stereoisomer, prepared from the β-isomer, had a C=C frequency of 1616 $cm^{-1}$ (Fig. 4). On the basis of this difference in frequency we consider that the stereoisomer of bis(2-acetoxy-1-methylpropenyl)mercury of m.p. 114° has the trans-trans configuration, and the other isomer has the cis-cis configuration. The absence of a third stereoisomer having the cis-trans configuration was proved by the fact that the reaction of the trans-trans isomer with mecuric chloride yielded only pure trans-2-acetoxy-1-methylpropenylmercury chloride and the reaction of the cis-cis isomer with the same reagent yielded only cis-2-acetoxy-1-methylpropenylmercury chloride without any trans-isomer as by-product.

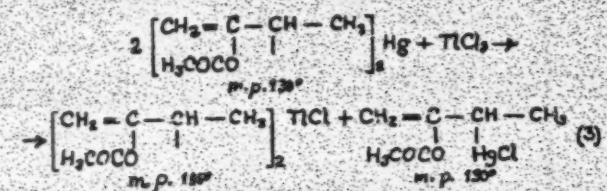
It has been shown previously [1] that the α-, β-, and γ-isomers are readily symmetrized to the corresponding fully substituted organomercury compounds. Each of these three symmetrical compounds (the cis-cis/trans-trans pair and their structural isomer) readily reacts with thallium trichloride in an ether medium, forming the corresponding disubstituted organothallium compound by the equation:



(1)

* At our request D. N. Shigorin determined the infrared absorption spectra, and we are very much indebted to him for this.





The organothallium compounds obtained by reactions (1), (2), and (3) are white crystalline substances melting respectively at 168°, 156°, amd 195°. They are soluble in alcohol, acetone, and hot water, but insoluble in benzene and ether. In each reaction, in addition to the disubstituted organothallium compound, the corresponding (α, β, or γ) organomercury compound is formed.

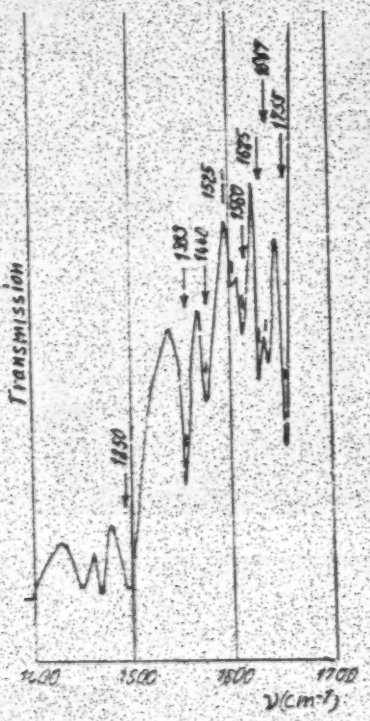



Fig. 1

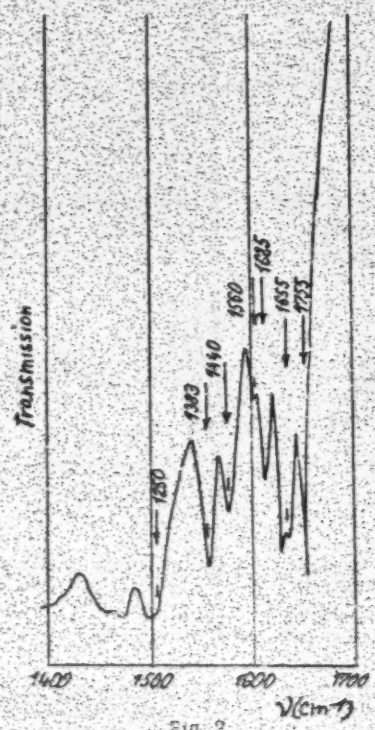
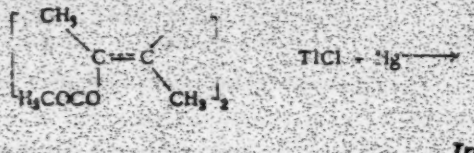



Fig. 2

The investigation of this reaction revealed that the stereoisomers of bis(2-acetoxy-1-methylpropenyl)mercury differed in their reactivities toward thallium trichloride: the trans-trans isomer is more reactive than the cis-cis isomer obtained from the β-compound. Reaction (1) proceeds instantaneously with evolution of heat, and the reaction product separates as a white crystalline precipitate; the reaction is quite complete in ten minutes. Reaction (2) proceeds more sluggishly without evolution of heat, and 40 minutes is required for its completion. We have thus again observed a difference in the rates at which the cis and trans isomers of organomercury compounds react [3]. We explain this difference by the higher degree of σ-conjugation in compounds in which there is a trans disposition of metal relative to an allenoid group [4].

The high-melting bis(2-acetoxy-1-methylpropenyl)thallium chloride reacts with mercury in acetone and yields the original trans-trans-bis(2-acetoxy-1-methylpropenyl)mercury, m.p. 114°.



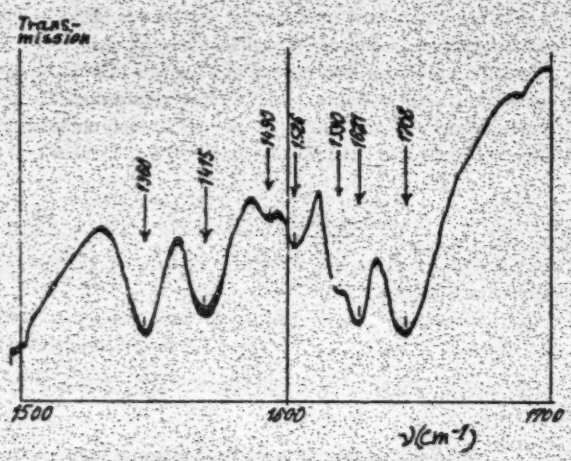




Fig. 3

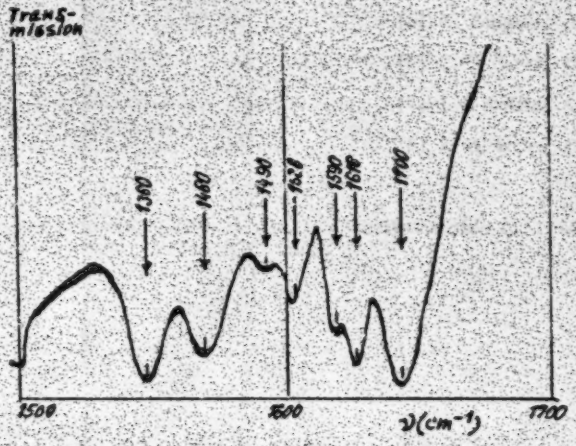
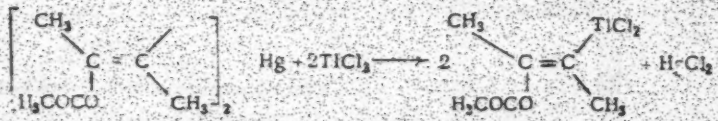



Fig. 4

The low-melting organothallium compound (m.p. 156°) reacts similarly with mercury, the sole product being cis-cis-bis(2-acetoxy-1-methylpropenyl)mercury (m.p. 101°).

We now describe also the preparation of monosubstituted organothallium compounds of the type $RTlCl_2$ from disubstituted mercury compounds and $TlCl_3$. The reaction of trans-trans-bis(2-acetoxy-1-methylpropenyl)mercury with $TlCl_3$ in a molar ratio of 1 : 2 proceeds according to the equation:

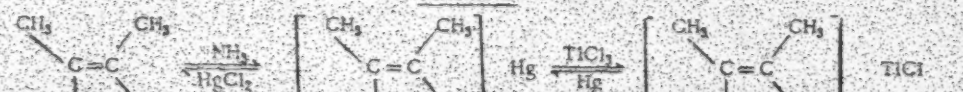



and yields a 2-acetoxy-1-methylpropenylthallium dichloride, a colorless crystalline substance, readily soluble in alcohol, acetone, and hot water, and insoluble in benzene and ether. It decomposes without melting at 141°. A second reaction product is mercuric chloride, which may be isolated as mercuric sulfide. Hence, in this reaction both organic residues pass from the mercury atom to the thallium atom; this behavior may be contrasted with that found in the preparation of $R_2TlCl$, in which the second product is an unsymmetrical organomercury compound. The cis-cis isomer reacts with $TlCl_3$ in a completely similar way and yields a 2-acetoxy-1-methylpropenylthallium dichloride that decomposes without melting at 135°. There is again a noteworthy difference in the rates of reaction, the reaction of the trans-trans isomer being the more rapid.

This investigation of geometric isomerism may be represented diagrammatically as follows.

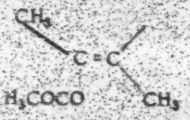
Scheme 1

Scheme 2

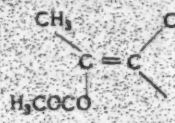



The configurations of the stereoisomers of 2-acetoxy-1-methylpropenylmercury chloride and of bis(2-acetoxy-1-methylpropenyl)mercury are known. Hence, the symmetrization reactions and the reverse reactions of dissymmetrization proceed with retention of the geometric configuration of the 2-acetoxy-1-methylpropenyl residue.

The exchange reaction between bis(2-acetoxy-1-methylpropenyl)mercury and $TlCl_3$ results in the formation of a pure organothallium compound melting at 16° and this reacts with mercury - evidently homolytically - and yields the pure original trans-trans organomercury compound. We may therefore assume either that the configuration of the



-group is retained throughout these reactions, or that it is reversed completely every time - as many times as is necessary so that there may be a return to the initial configuration. The second alternative is obviously very unlikely. In a similar way it can be shown that the reactions represented in Scheme 2 for the cis-compounds proceed with retention of the configuration of the



residue.

This investigation of the stereoisomers of organometallic compounds of the ethylene series therefore provides further confirmation of our proposed rule relating to the retention of geometric configuration in electrophilic and radical substitution reactions [5].

In this communication we describe also part of the experimental work that we have discussed previously [1].

## EXPERIMENTAL

### Synthesis of trans-2-Acetoxy-1-methylpropenylmercury Chloride

A solution of 7 g (0.02 mole) of mercuric acetate in 25 ml of glacial acetic acid was cooled to -18° and 1.2 g (0.02 mole) of 2-butyne (b.p. 28°), previously cooled with a mixture of ice and salt, was added. The reaction mixture was allowed to stand in a sealed glass tube at room temperature. After 24 hours the tube was cooled with ice and salt and then opened. The precipitate of mercurous acetate was separated and dried (0.20 g, i.e. 3.5% of the theoretical amount). The filtrate was treated with saturated aqueous potassium chloride. The resulting precipitate was separated and recrystallized from carbon tetrachloride. Crystals that separated at room temperature melted at 140°; the yield was 5.4 g (70%).

| | | | | | |
|---|---|---|---|---|---|
| | | Found % | C 20.61, 20.55; | H 2.59, 2.64; | Hg 57.74 |
| $C_6H_9O_2HgCl$ | Calculated % | C 20.62, | H 2.59 | Hg 57.46 | |

When the filtrate was cooled 0.4 g (5%) of a substance of m.p. 95-96° separated. From the acetic acid filtrate 1 g (1.4%) of mercury sulfide was obtained.

It was found that treatment of the filtrate with saturated aqueous sodium bromide gave the corresponding bromide, m.p. 162-163°, in 65% yield.

| | | | | | |
|---|---|---|---|---|---|
| | | Found % | C 18.48, 18.36; | H 2.32, 2.36; | Br 20.61, 20.40, Hg 50.66, 50.76 |
| $C_6H_9O_2HgBr$ | Calculated %: | C 18.29, | H 2.28 | Br 20.31, Hg 50.91 | |

It was also possible to isolate a compound of m.p. 105° in 10% yield.

| | | | | |
|---|---|---|---|---|
| | Found % | C 17.72, 17.60; | H 2.53, 2.31 | |
| $C_6H_9O_2HgBr$ | Calculated % | C 18.29; | H 2.28 | |

### Synthesis of cis-2-Acetoxy-1-methylpropenylmercury Chloride

The same amounts of starting materials were allowed to stand for 24 hours and then heated at 56° for two hours. The amount of mercurous acetate separated was 0.8 g (4.5%). The filtrate was treated as before. The precipitate formed was recrystallized from a mixture of ligroin and benzene (2 : 1). The crystals were filtered off and recrystallized twice, m.p. 145°, yield 2.4 g (4.4%). The filtrate was reduced in bulk by evaporation, and more crystals (needles) separated. When recrystallized from ligroin (110-130°), they melted at 95-96°, and further recrystallizations did not affect the melting point. Yield 3.88 g (40.4%).

| | | | | | |
|---|---|---|---|---|---|
| | | Found % | C 20.95, 20.83; | H 2.66, 2.73; | Hg 57.28 |
| $C_6H_9O_2HgCl$ | Calculated % | C 20.62; | H 2.59; | Hg 57.46 | |

A fraction of b.p. 95-110° was distilled from the acetic acid solution. On reaction with 0.5 g of p-nitrophenylhydrazine this gave a crystalline orange substance of m.p. 126°, raised to 126-127° by recrystallization from alcohol. A mixture test with authentic 2-butanone p-nitrophenylhydrazone showed no depression. From the residue in the distilling flask 2.96 g of mercury sulfide was obtained (37.6% on the amount of mercuric acetate taken for reaction).

Preparation of 2-Acetoxy-1-methylallylmercury Chloride

To a solution of 13 g (0.04 mole) of mercuric acetate in 39 ml of glacial acetic acid cooled to −18°, 2.2 g (0.04 mole) of 2-butyne was added. The mixture was heated in a sealed tube at 76° for 2 hours 30 minutes. The isolation of the reaction products was carried out under conditions similar to those used in the above-described experiments. The amount of mercurous acetate isolated was 1 g (9.5 %). Two recrystallizations of the organomercury chloride yielded 2.4 g (17%) of a product melting at 130°.

| | | | | | |
|---|---|---|---|---|---|
| | | Found %: | C 20.44; 20.61; | H 2.63; 2.72; | Hg 57.30 |
| $C_6H_9O_2HgCl$. | | Calculated %: | C 20.62; | H 2.59; | Hg 57.46 |

From the acetic acid filtrate 3.45 g (40.5%) of 2-butanone p-nitrophenylhydrazone (m.p. 127°) was obtained. In a mixture test with authentic 2-butanone p-nitrophenylhydrazone it showed no depression. From the residue in the distilling flask 2.7 g of HgS (28% on the amount of mercuric acetate taken for reaction) was obtained. The corresponding bromide, m.p. 127-128°, was also isolated.

| | | | | | |
|---|---|---|---|---|---|
| | | Found %: | C 18.50; 18.69; | H 2.43; 2.54; | Br 20.41; 20.31; Hg 50.83; 50.79 |
| $C_6H_9O_2HgBr$. | | Calculated %: | C 18.29; | H 2.28; | Br 20.31; Hg 50.98 |

Ozonization of 2-Acetoxy-1-methylallylmercury Chloride

2-Acetoxy-1-methylallylmercury chloride (10 g; m.p. 130°) was ozonized in dry chloroform (40 ml) for six hours with ozonized oxygen (6% of ozone), which was passed at 4 liters per hour. The white crystalline precipitate that formed before the ozonide was decomposed with water gave the characteristic yellow of hydrated mercuric oxide. The decomposition was effected by addition of 50 ml of water to the ozonide, together with the precipitate, and heating of the mixture in a water bath at 60° for six hours. The crystalline precipitate was separated, washed, and dried.

| | | |
|---|---|---|
| | Found%: | Hg 84.79 |
| $Hg_2Cl_2$. | Calculated%: | Hg 84.96 |

The filtrate was carefully neutralized with sodium carbonate. The chloroform layer was separated, and the aqueous layer was extracted with ether. The ether and chloroform extracts were united, dried with potassium carbonate, and transferred to a crystallizing dish. After the solvent had been evaporated off in the crystallizing dish, no reaction products could be detected. It was shown by the calomel method that formate was present in the aqueous solution of salts of organic acids. The greater part of this solution was evaporated to dryness on a water bath. A test by the cacodyl method on a small portion of the residue proved the presence of acetate. The remainder of the residue was treated with 10% hydrochloric acid solution, and the organic acids were extracted with ether. The extract was dried with sodium sulfate, and the ether was driven off. The residue was acidified with dilute sulfuric acid, and volatile acids (formic and acetic) were steam-distilled off, leaving behind any lactic acid that might be present.

The distillate was neutralized with sodium carbonate and heated with an aqueous solution of mercuric chloride. The glistening precipitate that formed—calomel—was filtered off, the solution was evaporated to dryness on a water bath, and the residue was acidified with 10% hydrochloric acid and extracted with ether. The liquid (1 g) remaining after removal of ether was heated with 1.1 g of thionyl chloride for 30 minutes in an oil bath at 100-120°. p-Toluidine (1.7 g) was carefully added to the mixture, and heating was continued at 120-130° for one hour. The liquid product obtained crystallized out when it was allowed to stand for one day over sulfuric acid in a desiccator. After two crystallizations from alcohol a product melting at 152° was obtained. A mixture test with p-acetotoluidide prepared by the same method showed no depression. The residue remaining after removal of volatile acids was filtered, and the solution was evaporated on a water bath. The syrupy residue was acidified with dilute sulfuric acid and repeatedly extracted with ether. Ether was distilled from the extract, 0.25 g of p-toluidine was added to the liquid residue (0.3 g), and the mixture was heated at 130-140° in an oil bath for two hours. The resulting liquid product solidified when cooled. Two recrystallizations from water yielded 0.5 g of the p-toluidide of lactic acid in the form of snow-white silky plates, m.p. 100.5-101.5°, undepressed by admixture of authentic p-toluidide of lactic acid (m.p. 101-102°).

Ozonization of cis- and trans-2-Acetoxy-1-methylpropenylmercury Chlorides

The ozonization of 7 g of 2-acetoxy-1-methylpropenylmercury chloride (m.p. 140°), the decomposition of

the ozonide, and the isolation of the reaction products were carried out under the conditions used in the preceding experiment. The chloroform and ether extracts contained no neutral products. No formate could be detected in the aqueous solution of salts of organic acids.

The aqueous solution was evaporated to dryness on a water bath. A small part of the dry residue was tested by the cacodyl test with arsenious oxide, and the presence of acetic acid was detected. Also, in order to confirm the presence of acetic acid, its p-toluidide, m.p. 152°, was obtained (no depression in a mixture test).

The ozonization of 2-acetoxy-1-methylpropenylmercury chloride (m.p. 95-96°), the decomposition of the ozonide, and the identification of the products was carried out as in the preceding experiments. Only acetic acid was detected in the products obtained by decomposing the ozonide. Acetic acid was proved by the cacodyl test and the preparation of its crystalline p-toluidide, m.p. 152°, undepressed by admixture of authentic p-acetotoluidide.

Reaction of Bis(2-acetoxy-1-methylpropenyl)mercury (M. p. 113°) with Thallium Trichloride

A solution of 0.18 g (0.0005 mole) of thallium trichloride in 5 ml of absolute ether was added at room temperature to a solution of 0.5 g (0.001 mole) of bis(2-acetoxy-1-methylpropenyl)mercury (m.p. 113°) in 10 ml of absolute ether. There was a slight rise in temperature, and a white crystalline precipitate was formed immediately. It was filtered off and washed three times with hot benzene. After recrystallization from aqueous alcohol it melted at 155-156° with decomposition. A further recrystallization did not affect the melting point. The yield was 0.26 g (96%). The substance was found to be soluble in acetone, alcohol, and hot water, and insoluble in ether, benzene, and petroleum ether.

The ether and benzene filtrates were evaporated under reduced pressure, and the dry residue was recrystallized twice from a mixture of petroleum ether (b.p. 90-110°) and benzene (2 : 1), when 0.38 g (95%) was obtained, m.p. 139-140°, undepressed by admixture of authentic 2-acetoxy-1-methylpropenylmercury chloride.

| | | | | | |
|---|---|---|---|---|---|
| | | Found %: | C 30.84; 30.94; | H 3.84; 3.75; | Cl 7.71; 7.69 |
| $C_{12}H_{19}O_4TlCl_2$ | Calculated %: | C 30.84; | H 3.86; | Cl 7.62 | |

Preparation of Bis(2-acetoxy-1-methylpropenyl)mercury Chloride having a Melting Point of 156°

A solution of 0.18 g (0.0005 mole) of thallium trichloride in 5 ml of absolute ether was added to a solution of 0.5 g (0.001 mole) of bis(2-acetoxy-1-methylpropenyl)mercury (m.p. 101-102°) in 30 ml of absolute ether. In this preparation the crystalline precipitate began to appear ten minutes after the ethereal solutions were mixed, and 45 minutes passed before the presence of thallium trichloride in the ethereal solution could no longer be detected.

The method of separating the reaction products was similar to that used in the preceding experiment. The precipitate, after being washed with benzene and recrystallized twice from alcohol, melted at 155-156° with decomposition. A further recrystallization did not affect the melting point. The yield was 0.26 g (96.7%).

| | | | | | |
|---|---|---|---|---|---|
| | | Found %: | C 30.77; 30.53; | H 3.96; 4.00; | Cl 7.97; 7.77 |
| $C_{12}H_{19}O_4TlCl_2$ | Calculated %: | C 30.84; | H 3.86; | Cl 7.62 | |

From the ether and benzene solutions 0.39 g (98%) of a substance of m.p. 90-95° was isolated. After recrystallization from petroleum ether it melted at 94-96°, undepressed by admixture of authentic 2-acetoxy-1-methylpropenylmercury of m.p. 98°.

Preparation of Bis(2-acetoxy-1-methylallyl)thallium Chloride

Reaction between 0.5 g (0.001 mole) of bis(2-acetoxy-1-methylallyl)mercury (m.p. 130°) with 0.18 g (0.0005 mole) of thallium trichloride in 5 ml of absolute ether was carried out under conditions similar to those of the previous experiments. A crystalline precipitate was formed immediately. It was washed with benzene and recrystallized from aqueous alcohol. The yield was 0.26 g (92.6%). When the crystals were heated in a sealed capillary, they blackened at 195° and had still not melted at 300°. The product was soluble in acetone, alcohol, and hot water, but insoluble in ether, benzene, and petroleum ether.

| | | | | | |
|---|---|---|---|---|---|
| | | Found %: | C 30.95; 30.82; | H 4.12; 4.05; | Cl 7.54; 7.59 |
| $C_{12}H_{19}O_4TlCl_2$ | Calculated %: | C 30.84; | H 3.86; | Cl 7.62 | |

From the ether and benzene filtrates 0.4 g (98%) of a substance melting at 120-129° was isolated. After recrystallization from a mixture of petroleum ether and benzene (2 : 1), it melted at 120-130°, and the melting point was not depressed by admixture of authentic 2-acetoxy-1-methylallylmercury chloride.

## Reaction of Bis(2-acetoxy-1-methylpropenyl)thallium Chloride of Melting Point 166° with Mercury

Mercury (2.3 g) and a solution of 0.25 g of bis(2-acetoxy-1-methylpropenyl)thallium chloride of m.p. 166° in 40 ml of acetone were placed in a two-necked cylindrical flask fitted with stirrer and reflux condenser. The reaction mixture was stirred vigorously at 60° for ten hours. The solution was separated from thallous chloride and unchanged mercury, and then evaporated to dryness. The residue was extracted with benzene, and after removal of the benzene, crystals melting at 107-111° were obtained.

After two recrystallizations from petroleum ether (b.p. 40-60°) they melted at 112-113°. A mixture with authentic bis(2-acetoxy-1-methylpropenyl)mercury melted at 112.5-113°. The yield of recrystallized product was 0.09 g (40.9%).

## Reaction of Bis(2-acetoxy-1-methylpropenyl)thallium Chloride of Melting Point 156° with Mercury

The reaction of 0.4 g of bis(acetoxy-1-methylpropenyl)thallium chloride of m.p. 156° with 3 g of mercury was carried out under conditions similar to those of the preceding experiment, and 0.18 g (50%) of a crystalline substance of m.p. 101° was isolated. There was no depression in a mixture test with previously synthesized bis(2-acetoxy-1-methylpropenyl)mercury.

## Synthesis of 2-Acetoxy-1-methylpropenylthallium Dichloride having a Decomposition Temperature of 141°

When ethereal solutions of 0.5 g (0.001 mole) of bis(2-acetoxy-1-methylpropenyl)mercury of m.p. 113° and of 0.72 g (0.002 mole) of thallium trichloride were mixed, there was an immediate white crystalline precipitate, which was filtered off after ten minutes, washed repeatedly with ether, and then recrystallized from water. When heated in a sealed capillary, the dried product blackened at 141° without melting; neither did it melt when recrystallized from aqueous alcohol or from water. The product was 0.85 g (93%) of 2-acetoxy-1-methylpropenylthallium dichloride. The substance is soluble in acetone, alcohol, and hot water, but insoluble in ether and benzene.

| | | | | | |
|---|---|---|---|---|---|
| | Found % | C 18.65, 18.56; | H 2.44, 2.47; | Cl 17.59, 17.57 |
| $C_6H_9O_2TlCl_2$. | Calculated % | C 18.53, | H 2.35; | Cl 18.28 |

The solvent was distilled from the filtrate obtained after separation of the 2-acetoxy-1-methylpropenylthallium dichloride, and the dry residue was dissolved in cold water. The solution was acidified with dilute hydrochloric acid and treated with hydrogen sulfide. The resulting precipitate of mercuric sulfide ($Tl_2S$ is not precipitated by hydrogen sulfide from acidified aqueous solution) was filtered off through a Gooch crucible and carefully washed with cold concentrated sulfuric acid to remove any possible $Tl_2S$ impurity. The precipitate was washed with water, with alcohol, and with ether, and dried at 110° to constant weight. The yield of HgS was 0.24 g, corresponding to 0.28 g of mercuric chloride (90% of the theoretical amount).

## Preparation of 2-Acetoxy-1-methylpropenylthallium Dichloride having a Decomposition Temperature of 135°

An ethereal solution of 2.16 g (0.006 mole) of thallium trichloride was added at room temperature to an ethereal solution of 1.5 g (0.003 mole) of bis(2-acetoxy-1-methylpropenyl)mercury of m.p. 101°. Separation of the crystalline precipitate did not begin until ten minutes had passed. After the mixture had stood for 40 minutes at room temperature, the precipitate was separated, washed with ether, and recrystallized from water. The yield of product was 80%. It decomposed at 135°, and after recrystallization from alcohol it still decomposed without melting at 135°. The substance readily dissolves when heated with alcohol, acetone, or water, but is of poor solubility in benzene and ether.

| | | | | | |
|---|---|---|---|---|---|
| | Found % | C 18.72, 18.85; | H 2.48, 2.55; | Cl 18.20, 18.05 |
| $C_6H_9O_2TlCl_2$. | Calculated % | C 18.53, | H 2.35; | Cl 18.28 |

Mercuric chloride was separated as in the previous experiment; 0.78 g of HgS was obtained, which corresponds to 0.9 g (94%) of $HgCl_2$.

## SUMMARY

1. On the basis of a study of their infrared absorption spectra, the α-isomer of 2-acetoxy-1-methylpropenylmercury chloride, which has a C=C frequency at 1667 $cm^{-1}$, is assigned the trans configuration, and its stereoisomer, which has a C=C frequency of 1655 $cm^{-1}$, is assigned the cis configuration.

2. Bis(2-acetoxy-1-methylpropenyl)mercury of m.p. 114°, which has a C=C frequency of 1621 $cm^{-1}$, has been assigned to the trans series, and its stereoisomer of m.p. 101°, which is obtained from the 3-compound and has a C=C frequency of 1616 $cm^{-1}$, has been assigned the cis-cis configuration.

3. Two new stereoisomeric bis(2-acetoxy-1-methylpropenyl)thallium chlorides have been synthesized from the stereoisomeric bis(2-acetoxy-1-methylpropenyl)mercurys and thallium trichloride, and some of their chemical properties have been investigated. Their geometric configurations have been established by the method of even and odd cycles.

4. It has been shown that the stereoisomeric bis(2-acetoxy-1-methylpropenyl)mercurys react at different rates with thallium trichloride, the trans-trans compound reacting much more rapidly than the cis-cis isomer.

5. A new reaction has been described in which organothallium compounds of the type $RTlCl_2$ are synthesized directly from symmetrical organomercury compounds and thallium trichloride.

6. By means of a symmetrization reaction bis(2-acetoxy-1-methylallyl)mercury has been prepared, and some of its chemical properties have been studied. It reacts with thallium trichloride with formation of bis(2-acetoxy-1-methylallyl)thallium chloride.

7. It has been shown that in the symmetrization and reverse dissymmetrization reactions, and also in the double-decomposition reactions with metal salts, the transfers of the 2-acetoxy-1-methylpropenyl group $CH_2{-}\underset{H_3COCO}{\overset{|}{C}}{=}\overset{|}{C}{-}CH_3$ from one metal atom to another and back occur without any change in geometric configuration. This behavior confirms the rule that we have established relating to the preservation of the configurations of cis and trans isomers in metathetic reactions with electrophilic reagents and in homolytic exchange reactions.

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# DECOMPOSITION AND FORMATION OF ONIUM SALTS AND THE SYNTHESIS OF HETERO-ORGANIC COMPOUNDS

## COMMUNICATION 8. DECOMPOSITION OF BENZENEDIAZONIUM FLUOBORATE IN PRESENCE OF NITRILES

L. G. Makarova and A. N. Nesmeyanov

We have shown in previous investigations [1, 2] that benzenediazonium and diphenyliodonium fluoborates decompose heterolytically. The heterolytic character of the decomposition of benzenediazonium fluoborate was proved by observations on the orientation of entering groups both in substitution reactions with benzene derivatives (the phenyl cation formed by the decomposition of benzenediazonium fluoborate was found to enter the meta position with respect to an orienting group of the second kind), and also in addition reactions with unsaturated compounds. In the present investigation we have studied the decomposition of benzenediazonium fluoborate in presence of nitriles.

It was thought that the phenyl cation formed by the decomposition of benzenediazonium fluoborate would add at the point of highest electron density in the nitrile molecule – the nitrogen of the nitrile group – with the formation of anilides, in accordance with the scheme:

$$RC\equiv N + C_6H_5^+ + F^- \longrightarrow RCF{=}NC_6H_5 \xrightarrow{H_2O} RC(OH){=}NC_6H_5 \rightleftharpoons RC(=O)-NHC_6H_5$$

Also, it could be expected that, as a result of the decomposition of benzenediazonium fluoborate in a medium of benzonitrile (or other aromatic nitrile), 3-biphenylcarbonitrile (or one of its homologs) would be formed by entry of the phenyl cation into the benzene nucleus in the meta position to the meta-orienting nitrile group.

On the other hand, the possibility could not be excluded that the diazonium form would be converted into the diazo form under the influence of the free pair of electrons on the nitrogen of the nitrile group, which is what actually occurs when benzenediazonium fluoborate decomposes in pyridine, in presence of hydroxyl ions, or in presence of metals:

$$C_6H_5N{=}N{:} + \cdot OH \longrightarrow C_6H_5N{=}N^{\cdot} \longrightarrow C_6H_5N{=}N-$$

The decomposition of the diazo form, however, would be homolytic, with formation of an aryl radical; and by reaction of this aryl radical with the nitrile, not only the anilide, but also other products would be formed, in particular ketones and, when aromatic nitriles are used, also derivatives of 2- or 4-biphenylcarbonitrile. The phenyl radical formed by the decomposition of benzenediazohydroxide enters the benzene nucleus in the para position to the nitrile group with formation of 4-biphenylcarbonitrile [3].

Hanby and Waters [4] found that, in the decomposition of benzenediazonium chloride in acetonitrile, a mixture of substances was formed – benzene, chlorobenzene, and about 10% of acetanilide – and this was interpreted by them as proof of the homolytic character of the decomposition of arenediazonium chlorides. When the decomposition was carried out in propionitrile, Hanby and Waters found only benzene and chlorobenzene in the products and could not detect any propionanilide. They were unable to identify any reaction products in the decomposition of benzenediazonium chloride in a medium of phenylacetonitrile.

In the decomposition of arenediazonium chlorides in aqueous acetone solution in presence of acrylonitrile, sodium acetate, and a cupric salt, Koelsch [5] obtained 30-40% yields of products of the addition of aryl at the double bond, namely, nitriles of $\alpha$-chlorohydrocinnamic acids. This must be considered to prove that the decomposition of the diazo compounds investigated by Koelsch is homolytic and is followed by addition of an aryl radical at a double bond. Koelsch did not observe addition of aryl to the nitrogen of acrylonitrile.

We have carried out the decomposition of benzenediazonium fluoborate in the following media: benzonitrile, p-tolunitrile, o-tolunitrile, phenylacetonitrile, acetonitrile, propionitrile, and acrylonitrile. It was found that phenyl added at the nitrogen of the nitrile group with formationof the corresponding anilides, the yields being 40 % from benzonitrile, p-tolunitrile, and phenylacetonitrile, 30 % from o-tolunitrile and acetonitrile, 15 % from propionitrile, and 10% from acrylonitrile. No ketone formation was observed in any of these reactions. In the reactions with aromatic nitriles, phenyl did not enter the aromatic nucleus – no biphenyl derivatives were formed. Also, when the decomposition occurred in a medium of acrylonitrile, no identifiable products arising by the addition of phenyl at the carbon-carbon double bond were obtained. Formation of anilides was accompanied by the polymerization of the nitriles, evidently resulting from the promoting action of boron trifluoride, and in the reactions with benzonitrile and p-tolunitrile the trimers were isolated; in the other reactions the occurrence of polymerization was shown by the formation of high-boiling substances or undistillable (acrylonitrile) resins.

The following facts, therefore, indicate that the mechanism of the reaction that we have investigated is different from that of the reactions of Hanby and Waters, Koelsch, and Gomberg and Bachmann, and that it consists, in fact, of the action of a phenyl cation, formed by the heterolytic decomposition of benzenediazonium fluoborate, on the nitrile: first, the greatly increased yields of anilides in the decomposition of benzenediazonium fluoborate in nitrile media, as compared with the yields obtained by Hanby and Waters in the decomposition of benzenediazonium chloride (for acetonitrile 10 to 20%, for phenylacetonitrile 0 to 40%, and for propionitrile 0 to 14%); second, the absence of ketone formation by the action of radicals on the nitriles; and finally, the formation of essentially different products (comparison of the decomposition of benzenediazonium fluoborate in acrylonitrile and benzonitrile media with the decomposition of arenediazonium chloride in acrylonitrile and benzenediazohydroxide in benzonitrile).

## EXPERIMENTAL

### Decomposition of Benzenediazonium Fluoborate in a Benzonitrile Medium

The decomposition was carried out in a four-necked cylindrical flask placed in an oil bath and fitted with mercury-sealed stirrer, reflux condenser, and thermometer. The fourth opening of the flask was used for the addition of the diazonium salt. Benzenediazonium fluoborate was freshly prepared and dried in a desiccator over calcium chloride; 150 g (one molecular proportion) of it was added in small portions over a period of 80 minutes to 225 g (2.8 molecular proportions) of benzonitrile at 70°. The reaction was exothermic, and after addition of the first portion of diazonium salt the temperature rose to 80°. Further additions were therefore made without external heating, the rate of addition being adjusted so that the temperature did not rise above 80°. The reaction mixture gradually darkened, white fumes were evolved, and deliquescent crystals containing boron trifluoride, formed in the condenser. When the addition of the diazonium salt was complete, the mixture was heated at 75° for 45 minutes. On the next day the mixture was dissolved in ether, the small amount of boron-containing inorganic precipitate being removed. When washed with 10% NaOH (500 ml), the ether solution yielded a voluminous precipitate, which was filtered off. From this precipitate, boiling ethanol extracted 33.4 g of benzanilide. After recrystallization from alcohol its melting point and the melting point of a mixture with known benzanilide were 163°. The alcohol-insoluble residue was crystallized from benzene and chloroform, and then melted at 232°. For kyaphenin (2,4,6-triphenyl-s-triazine) $(C_6H_5C)_3N_3$ Scholl and Norr [6] give m.p. 231-232°.

The ether solution was washed with water and dried with sodium sulfate. The residue remaining after removal of ether was vacuum-distilled.

Fraction I, b.p. 74-76° (12 mm), 98 g
Fraction II, b.p. 120-167° (5 mm), 1 g
Fraction III, b.p. 185-205° (5 mm), 30 g
Fraction IV, b.p. 205-255° (5 mm), 13 g

Fraction I was benzonitrile. Fraction III solidified completely. Fraction IV was a viscous red oil, which partially solidified on standing. The crystals that formed from Fraction IV were separated from the oil and added to Fraction III. The mixture was crystallized from alcohol, acetone, or benzene, and the melting point of the product, and also of its mixture with known benzanilide, was 163°. The total yield of benzanilide was 81 g (39%).

Found %: C 78.94; 79.14; H 5.05; 5.52
$C_{13}H_{11}ON$ Calculated %: C 79.16; H 5.61

Solvent was distilled from the mother liquor remaining from the crystallization of benzanilide, and the

residue was boiled with concentrated hydrochloric acid for three days. The hydrochloric acid solution was steam-distilled. Part of the distillate was extracted with ether, and the residue remaining after removal of ether from the extract was sublimed. The melting points of the product and of a mixture of it with benzoic acid were 121°. The remainder of the distillate was rendered alkaline and again steam-distilled; the new distillate was extracted with ether, and the ether extract was dried. After removal of ether a very small greasy residue remained, and this gave no precipitate with 2,4-dinitrophenylhydrazine.

### Decomposition in a p-Tolunitrile Medium

Over a period of 75 minutes, 137 g (one molecular proportion) of benzenediazonium fluoborate was added in small portions to 143 g (1.7 molecular proportions) of p-tolunitrile heated to 70° in an oil bath. Reaction was exothermic, and the decomposition was carried out at 75-76° without external heating. When the addition of the diazonium salt was complete, the mixture was stirred for one hour in an oil bath at 70-75°. On the next day, the whole of the thick dark-colored mass was dissolved in ether, and the resulting solution was washed with 10% NaOH. A precipitate was then formed, and this, together with the ether layer, was washed with water. The ether was distilled off, and p-tolunitrile was vacuum-distilled from the residue. The semisolid substance that remained was vacuum-distilled, and boiled over the range 188-248°. The residue crystallized completely during the distillation. In its recrystallization from ethanol 5.7 g of alcohol-insoluble residue was obtained, and this, after crystallization from benzene and chloroform, melted at 280-281° (Francis and Davis [7] give m.p. 278° for 2,4,6-tri-p-tolyl-s-triazine).

Found %: C 81.98; 82.38; H 5.99; 6.02
$C_{24}H_{21}N_3$. Calculated %: C 82.05; H 5.98

The ethanol solution yielded 57.8 g of a substance melting at 142°, alone and in admixture with known p-toluanilide. The yield was 40.5%.

### Decomposition in an o-Tolunitrile Medium

Over a period of 90 minutes, 120 g (one molecular proportion) of benzenediazonium fluoborate was added to 125 g (1.7 molecular proportions) of o-tolunitrile heated to 70°. The temperature was maintained at 70-72° by the heat of reaction. When the whole of the benzenediazonium fluoborate had been added, the mixture was stirred at the same temperature for 90 minutes. On the next day the dark-colored reaction mass was dissolved in ether, and the solution was washed with 10% NaOH and water. Ether and water were distilled off, and the residue was vacuum-distilled.

Fraction I, b.p. 65-74° (5 mm)
Fraction II, b.p. 200-220° (5 mm); 31.14 g
Fraction III, b.p. 212-268° (5 mm); 12.3 g

Fraction I was o-tolunitrile. Fraction II solidified; Fraction III came over toward the end as a noncrystallizing oil. Fractions II and III were combined and crystallized from ethanol, and 40 g (30.3 %) was obtained of a substance melting at 125° (reported melting point of o-toluanilide, 125° [8]).

### Decomposition in a Phenylacetonitrile Medium

Over a period of 75 minutes, 120 g (one molecular proportion) of benzenediazonium fluoborate was added to 200 g (2.7 molecular proportions) of phenylacetonitrile heated to 70°. The decomposition was carried out at 68-72° without external heating. When the whole of the diazonium salt had been added, the mixture was heated for one hour at 70°. On the next day the dark-colored oil was dissolved in ether—there was a small amount of ether-insoluble orange-red resinous residue. The ether solution was washed with 10% NaOH solution and with water; it was then dried with sodium sulfate. Ether was distilled off, and o-tolunitrile was removed under reduced pressure (b.p. 105-109° at 12 mm). Vacuum fractionation of the residue yielded Fraction I (200-240°/5 mm), 42 g and Fraction II (242-295°/5 mm), 16.3 g.

Fraction I solidified completely. Fraction II was a dark red oil that partially solidified, and crystals were separated from the oil and added to Fraction I. Recrystallization of this mixture from ethanol yielded 48 g (39%) of a substance melting at 116° after recrystallization from benzene (the reported melting point of 2-phenylacetanilide is 116° [9]).

A test for ketone, carried out as in the experiment on benzonitrile, was negative.

### Decomposition of an Acetonitrile Medium

Over a period of 20 minutes, 96 g (one molecular proportion) of benzenediazonium fluoborate was added to 161 g (7.3 molecular proportions) of acetonitrile heated to 72°. Decomposition occurred with vigorous foaming and slight fuming, and the temperature was maintained at 72° without external application of heat. When the whole of the benzenediazonium fluoborate had been added, the stirred mixture was heated at 72-76° for one hour. It was then dissolved in ether, and the ether solution was washed with 10% NaOH and with water; it was then dried with sodium sulfate. After removal of ether and excess of acetonitrile by distillation 27 g of an oil remained; it solidified when cooled. Vacuum distillation yielded:

Fraction I. b.p. 150-175° (7 mm); 20 g
Fraction II. b.p. 240-265° (7 mm); 1.82 g

A small amount of black resin remained in the flask. Fraction I solidified completely and, when crystallized from water, it yielded 16.3 g of white leaves melting alone and in admixture with acetanilide, at 114°. Fraction II was a red, viscous mass, from which a little acetanilide separated on standing.

The alkaline wash liquors were acidified and extracted with ether, when a further 3.35 g of acetanilide m.p. 114, was obtained. The total yield of acetanilide was 19.7 g (29%). Fraction II and the mother liquors from the crystallization of acetanilide were tested for the presence of ketone as in the experiment on benzonitrile. No precipitate was formed with 2,4-dinitrophenylhydrazine.

### Decomposition in a Propionitrile Medium

One molecular proportion (43 g) of benzenediazonium fluoborate was added in small portions to 35 g (three molecular proportions) of propionitrile heated to 68°. Addition of the first portion of the diazonium salt caused the temperature to rise to 78°; further additions were made at 70-75°. When the whole of the diazonium salt had been added, the mixture was stirred for one hour at 75°. On the next day the mixture was dissolved in ether. The ether solution was washed with 10% NaOH and with water, and was dried with sodium sulfate. Ether was distilled off, and the excess of propionitrile was distilled off under reduced pressure.

Fraction I. b.p. 65- 90° (6 mm); 0.83 g
Fraction II. b.p. 90-150° (6 mm); a few drops
Fraction III. b.p. 150-155° (6 mm); 5.64 g

Fraction III solidified completely. After being crystallized from benzene it melted at 105° (the reported melting point of propionanilide is 105° [10]). The yield was 5.08 g (15%).

### Decomposition in an Acrylonitrile Medium

Over a period of one hour, 73 g (one molecular proportion) of benzenediazonium fluoborate was added in small portions to 80 g (four molecular proportions) of acrylonitrile heated to 70°. Toward the end of this time a precipitate of resin formed and the mixture foamed strongly. After addition was complete the mixture was stirred at the same temperature for 15 minutes. The reaction mixture consisted of an oil and a lump of red resin. The oil was extracted with ether and the resin was washed with ether, and the combined ether solutions were washed with 10% NaOH and with water, and were then dried with sodium sulfate. After removal of ether, there remained an oil which slowly crystallized. The oil was distilled from a pear-shaped flask, and yielded 5.9 g (10.7 %) of an oil, b.p. 145-150° at 3 mm, which rapidly solidified. After being crystallized from acetone it melted at 105°, the reported melting point of acrylanilide is 104-105° [11]. The residue in the flask was a dark-brown resin.

### SUMMARY

1. By the decomposition of benzenediazonium fluoborate in a nitrile medium (benzonitrile, p- and o-tolunitriles, phenylacetonitrile, acetonitrile, propionitrile, and acrylonitrile), the corresponding anilides have been obtained in yields of up to 40%.

2. The occurrence of this reaction provides confirmation of the heterolytic character of the decomposition of benzenediazonium fluoborate.

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# NEW METHOD FOR THE SYNTHESIS OF 1-AMINOALKYL-PHOSPHONIC AND -PHOSPHINIC ACIDS

## COMMUNICATION 4. SYNTHESIS OF (1-AMINOALKYL)PHENYLPHOSPHINIC ACIDS

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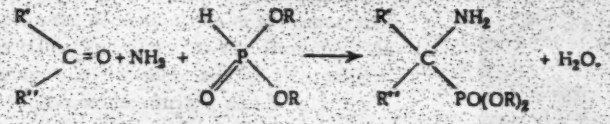
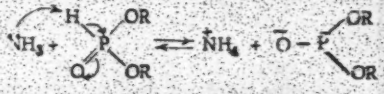
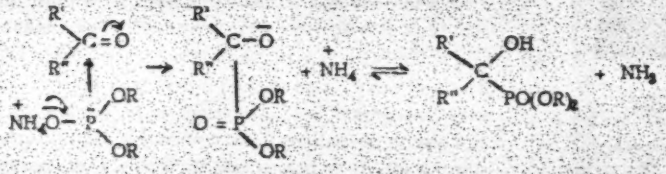
In previous communications [1] we have shown that a dialkyl hydrogen phosphite, an aldehyde or ketone, and ammonia will react together and yield a 1-aminoalkylphosphonic ester:



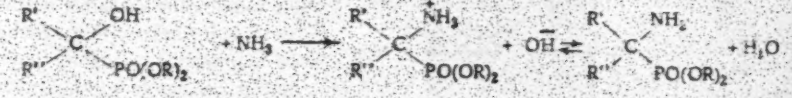
We treated the mechanism of this reaction as follows. We considered that the dialkyl phosphite ionizes in presence of ammonia, with transfer of reaction center and formation of a phosphite anion containing tervalent phosphorus:



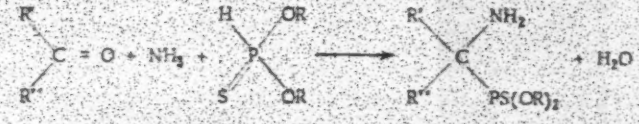
and this then adds to the carbonyl compound:



after which hydroxyl is replaced by amino:



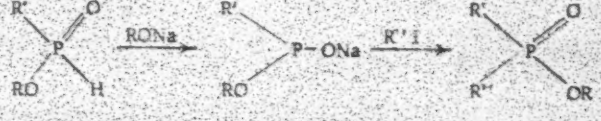
We then suggested that reactions of this type should be possible for the ammonium salts of all acids capable of diad or triad tautomerism [2]. For example, dialkyl phosphorothioites are acids of this type [3]. For this reason, these substances, as we have shown in our laboratory [4], react with carbonyl compounds and ammonia with formation of the corresponding esters of 1-aminoalkylphosphonothionic acids:



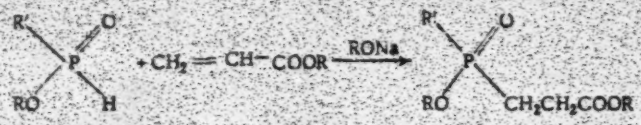
Monoesters of aryl (or alkyl) phosphonous acids are of the same type:

$$C_6H_5-POH(OR) \text{ or } C_6H_5-POH(OR).$$

These substances are able to form metal derivatives, which react with alkyl halides by a reaction of the Michaelis-Becker type [5]:

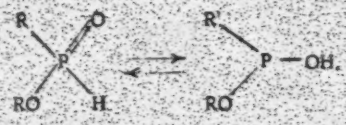


in presence of alkaline catalysts they add to an activated double bond, for example that of an acrylic ester [6]:

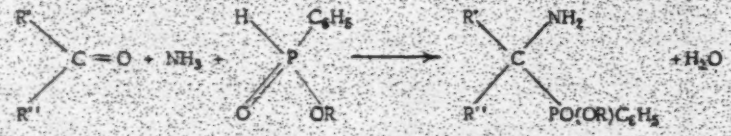


and they add also to carbonyl compounds with formation of alkyl(1-hydroxyalkyl)phosphinic esters:

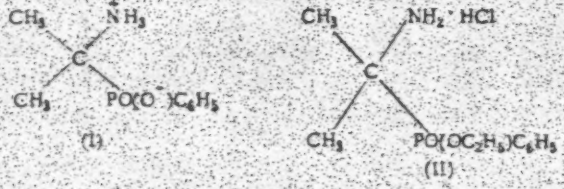
and they show all the other properties of diad-tautomeric substances:



There was every reason to expect, therefore, that monoesters of phenylphosphonous acid would react with carbonyl compounds in presence of ammonia with formation of the corresponding esters of (1-aminoalkyl)phenylphosphinic acids:



It was in fact found that, when a mixture of acetone, ethyl hydrogen phenylphosphonite, and alcoholic ammonia was heated in a sealed tube in a boiling water bath for three hours, reaction occurred in accordance with the foregoing scheme, and the product was undoubtedly ethyl (1-amino-1-methylethyl)phenylphosphinate. If, however, alcohol and (under reduced pressure) unchanged ethyl phenylphosphinite were distilled from the reaction mixture, only a



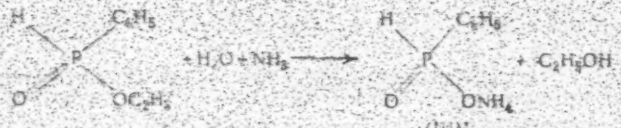
(I) (II)

very small amount of this ester could be isolated (as its hydrochloride II). The main product isolated was the acid (internal salt),

The same free acid is obtained when butyl phenylphosphonite is used instead of the ethyl ester. Reduction in the duration of heating results in only a slight increase in the yield of ester. It may be supposed that the ester formed in the reaction is decomposed by heat:

The low yield of ester may be explained also by partial hydrolysis of the original phosphonous ester.

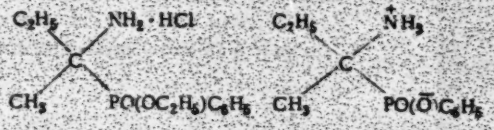
It is in fact found that the ammonium salt of free phenylphosphonous acid (III) can always be found in the reaction products; it is formed by the hydrolysis of the original ester:



(III)

When the reaction between acetone, ethyl hydrogen phosphonite, and alcoholic ammonia is carried out at 150°, instead of 100° this ammonium hydrogen phosphonite (III) is the main product.

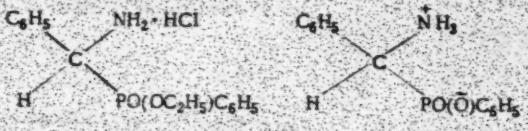
In the reaction with 2-butanone, carried out in a boiling water bath for six hours, the main reaction product was ethyl (1-amino-1-methylpropyl)phenylphosphinate, isolated as its hydrochloride (IV):



(IV) (V)

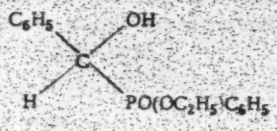
but when the duration of heating was 12 hours, only the free acid (V) could be isolated. The same acid was obtained by the hydrolysis of (IV).

The reaction between benzaldehyde, ethyl hydrogen phosphinate, and alcoholic ammonia resulted in the formation of ethyl (α-aminobenzyl)phenylphosphinate [its hydrochloride is (VI)], which was hydrolyzed to the free acid (VII):



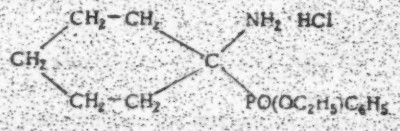
(VI) (VII)

Under milder conditions the hydroxy derivative (VIII) is obtained instead of the amino compound:



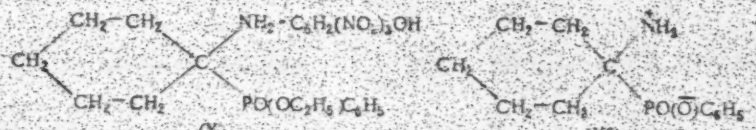
(VIII)

Cyclohexanone will also take part in this reaction with formation of ethyl(1-aminocyclohexyl)phenylphosphinate [the hydrochloride is (IX)]:



(IX)

The hydrochloride was converted into the free ester by treatment with sodium carbonate, and the ester was converted into its picrate (X). Hydrolysis of the hydrochloride (IX) with hydrochloric acid at 115-125° (sealed tube) yielded free (1-aminocyclohexyl)phenylphosphinic acid (XI):

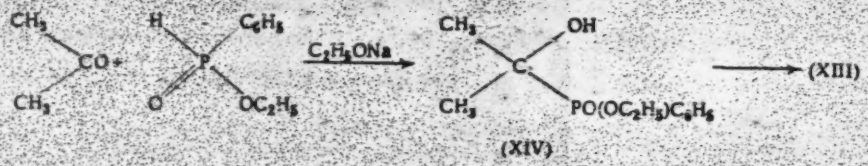


(X) (XI)

In proving the structure of the amino phosphinic acids, we took (1-amino-1-methylethyl)phenylphosphinic acid as our working example. The presence of a free amino group was proved by acetylation of the acid to (1-acetamido-1-methylethyl)phenylphosphinic acid (XII) and by treatment with nitrous acid, which yielded the corresponding hydroxy acid (XIII):

(XII) (XIII)

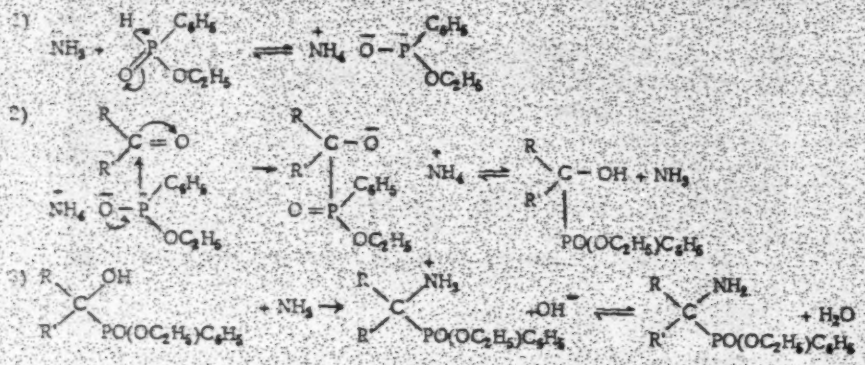
We synthesized the same acid following Abramov [7] by addition of ethyl hydrogen phenylphosphonite to acetone and hydrolysis of the resulting ester (XIV):



(XIV)

The melting points of the two preparations of (1-hydroxy-1-methylethyl)phenylphosphinic acid were the same; there was no melting point depression when they were mixed.

We consider that the mechanism of the reaction described in the present paper is similar to that proposed by us for the reaction between a dialkyl phosphite, a carbonyl compound, and ammonia. We give it here without explanation.



We consider that similar reactions can occur also for monoesters of other alkyl- and aryl-phosphonous acids.

## EXPERIMENTAL

### 1-Amino-1-methylethyl)phenylphosphinic Acid (I)

a) A mixture of 4 g of acetone, 11.5 g of ethyl hydrogen phenylphosphonite (prepared from phenylphosphonous dichloride and ethanol [5, 6], b.p. 116-117°/4 mm; $n_D^{20}$ 1.5223), and 15 ml of a 10% solution of ammonia in absolute ethanol was heated in a sealed tube in a boiling water bath for three hours. Alcohol and excess of ammonia were removed under reduced pressure, the mixture being heated in a boiling water bath. The residue was fractionated, and 8 g of a clear colorless liquid came over at 115-117° and 4 mm; it was found to be unchanged ethyl hydrogen phenylphosphonite containing some substance of alkaline reaction as impurity. The residue in the flask became very thick, and it partially crystallized; it was dissolved in a small amount (2-3 ml) of boiling absolute ethanol. The solution was cooled, and the crystals that appeared were filtered off. Recrystallization from alcohol yielded 3.2 g of a colorless crystalline substance, melting with decomposition at 244°. The yield was 24% (or, calculated on the amount of the phenylphosphonous ester that reacted, 79%).

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| | Found % | C 53.9; 54.3; | H 6.7; 6.7; | P 15.6; 15.5; | N 7.2; 7.3 |
| $C_9H_{14}PNO_2$ (I). | Calculated %: | C 54.3; | H 7.0; | P 15.6; | N 7.0 |

An aqueous solution of (1-amino-1-methylethyl)phenylphosphinic acid is neutral to litmus.

The distillate obtained from the reaction product was dissolved in dry ether, and dry hydrogen chloride was passed through the solution. The crystals that were precipitated (0.3 g) were reprecipitated from an alcohol-ether mixture, and then melted with decomposition at 186°.

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| | Found % | C 50.3; 50.6; | H 7.0; 7.2; | P 12.1; 12.1; | N 5.5; 5.4 |
| $C_{11}H_{19}NPO_2Cl$ (II) | Calculated %: | C 50.1; | H 7.2; | P 11.8; | N 5.3 |

When the above-described synthesis was carried out under milder conditions (one hour at 100° or 20-25 days at 20°), a somewhat greater amount of ethyl (1-amino-1-methylethyl)phenylphosphinate was obtained, but the total yield was not increased.

Under more severe conditions (nine hours at 100° or three hours at 150°) no ethyl (1-amino-1-methylethyl)phenylphosphinate was obtained; the only product was ammonium hydrogen phenylphosphonite (III). In these experiments, after removal of alcohol and excess of ammonia from the reaction mixture, 2 ml of absolute ethanol was added to the residue, and this was followed by the addition of ether. The precipitate that then formed was filtered off. Reprecipitation from a mixture of alcohol and ether yielded 0.9 g of a colorless substance melting at 175°. It was readily soluble in water, and it yielded ammonia when treated with alkali.

| | | | | | | |
|---|---|---|---|---|---|---|
| | | Found % | C 45.4; 45.2; | H 6.2; 6.5; | P 19.6; 19.5; | N 8.1; 8.1 |
| $C_6H_{10}NPO_2$ (III). | Calculated % | C 45.3 | H 6.3 | P 19.5 | N 8.8 | |

b) When a mixture of 4 g of acetone, 13.2 g of butyl hydrogen phenylphosphonite (b.p. 120-121° at 4 mm; $n_D^{20}$ 1.5077) and 15 ml of a 10% solution of ammonia in ethanol was heated in a sealed tube in a boiling water bath for three hours, the same amount of (1-amino-1-methylethyl)phenylphosphinic acid was obtained as in the experiment described above.

(1-Amino-1-methylpropyl)phenylphosphinic Acid (V)

a) A mixture of 4.8 g of 2-butanone, 11.5 g of ethyl hydrogen phenylphosphonite, and 20 ml of a 10% solution of ammonia in absolute ethanol was heated in a sealed tube in a boiling water bath for 12 hours. On cooling, the solution yielded a colorless crystalline precipitate (0.2 g), which was filtered off and found to be ammonium hydrogen phenylphosphonite (III). Volatile substances and unchanged ethyl hydrogen phenylphosphonite (5 g) were then distilled off, and the residue was dissolved in hot alcohol. The crystals that appeared when the solution cooled were filtered off and recrystallized from alcohol. The product formed colorless crystals (yield 17% or 30% calculated on the amount of phenylphosphonous ester that reacted). After being dried in a vacuum desiccator over phosphoric oxide, the substance melted with decomposition at 197-198°. It was very hygroscopic, and was neutral to litmus.

| | | | | |
|---|---|---|---|---|
| | Found % | N 6.5; 6.4; | P 14.4; 14.5 | |
| $C_{10}H_{16}NPO_2$ (V). | Calculated % | N 6.6; | P 14.6 | |

b) A mixture of 4.8 g of 2-butanone, 11.5 g of ethyl hydrogen phenylphosphonite, and 20 ml of 10% alcoholic ammonia was heated in a boiling water bath for six hours. Alcohol and ammonia were then removed under reduced pressure, and ether was added to the residue. The precipitate formed was filtered off (1.5 g of ammonium hydrogen phenylphosphonite), and dry hydrogen chloride was passed through the solution. An oil was thrown out, and this finally solidified after standing for three days and being rubbed in presence of dry ether. The substance was reprecipitated from an alcohol-ether mixture. The product was 8 g of (IV), m.p. 156-157°. It was difficult to purify (from ammonium chloride and the hydrochloride of the acid) and the analytical results were somewhat low.

The hydrochloride (IV) was hydrolyzed with hydrochloric acid in sealed tubes (three hours at 120-130°). The solution was evaporated on a water bath, and in order to remove hydrochloric acid from the residue, the latter was again dissolved in water, accurately neutralized, and evaporated to dryness. The dry residue was extracted with hot ethanol. Crystallization from alcohol yielded a substance melting at 197-198° (yield about 30%).

Hydrochloride of Ethyl (α-Aminobenzyl)phenylphosphinic Acid (VI)

A mixture of 7 g of benzaldehyde, 11.5 g of ethyl hydrogen phenylphosphonite, and 17 ml of a 10% solution of ammonia in absolute ethanol was heated in a sealed tube in a boiling water bath for 12 hours. Alcohol and excess of ammonia were then removed under reduced pressure, and dry ether was added to the residue. The precipitate formed (4.8 g) was filtered off; it was found to be ammonium hydrogen phenylphosphonite (III). Dry hydrogen chloride was passed through the ether solution. The oil that separated crystallized partially after it had stood for three days. After prolonged rubbing with fresh portions of dry ether, the oil solidified completely. Recrystallization from a mixture of alcohol and ether yielded 5.4 g (26%) of a substance melting at 164-165°.

| | | | | |
|---|---|---|---|---|
| | Found % | P 9.9; 9.7; | N 4.6; 4.5 | |
| $C_{15}H_{19}NPO_2Cl$ (VI). | Calculated % | P 9.9; | N 4.5 | |

When the reaction is carried out under milder conditions, the main product is ethyl (α-hydroxybenzyl)phenylphosphinate (VIII). Thus, the same mixture of reactants was heated for five hours, and 2 g of ethyl (α-hydroxybenzyl)phenylphosphinate, m.p. 75°, was isolated.

| | | | | | | |
|---|---|---|---|---|---|---|
| | | Found % | C 65.9; 65.5; | H 5.7; 5.8; | P 11.1; 11.1 | |
| $C_{15}H_{17}PO_3$. | | Calculated % | C 65.2; | H 6.2; | P 11.2; | |

In this experiment the yield of the hydrochloride of ethyl (α-aminobenzyl)phenylphosphinate was only about 10%.

(4-Aminobenzyl)phenylphosphinic Acid (VII)

A mixture of 4 g of the hydrochloride prepared as above and 80 ml of 1 : 1 hydrochloric acid was heated at 125-130° in two sealed tubes for three hours. The contents of the tubes were then evaporated down until a residue of constant weight was obtained. Recrystallization of the residue from 50% ethanol yielded 1.6 g (48%) of a colorless crystalline substance, m.p. 218°. The substance crystallized with one molecule of water of crystallization.

Found %: C 58.8; 58.8; H 5.8; 6.1; P 11.5; 11.2; N 5.3; 5.2; $H_2O$ 5.8; 6.7

$C_{13}H_{14}NPO_3 \cdot H_2O$ (VII). Calculated %: C 58.9; H 6.1; N 5.3; P 11.7; $H_2O$ 6.8

Hydrochloride of Ethyl (1-Aminocyclohexyl)phenylphosphinate (IX)

A mixture of 6.5 g of cyclohexanone, 11.5 g of ethyl hydrogen phenylphosphonite, and 17 ml of a 10% solution of ammonia in absolute alcohol was heated in sealed tubes in a boiling water bath for 12 hours. Alcohol and excess of ammonia were distilled off, and dry ether was added to the residue. The crystals that had formed in the solution by the next day were filtered off (1.2 g); they were found to be ammonium hydrogen phenylphosphonite. Dry hydrogen chloride was passed through the ether solution and an oil separated which partially crystallized after standing for three days. The oil was repeatedly rubbed out in presence of fresh portions of ether, and finally a free-running solid was obtained, which was reprecipitated from an alcohol-ether mixture. The yield was 6.2 g (31%). The substance had a double melting point, 149° and 193°. It was hygroscopic.

Found %: N 4.6; 4.4; P 9.8

$C_{14}H_{23}NPO_2Cl$ (IX) Calculated %: N 4.6; P 10.2

Picrate of Ethyl (1-Aminocyclohexyl)phenylphosphinate (X)

A saturated solution of sodium carbonate was added to a solution of 5.0 g of the hydrochloride (IX) in 10 ml of water. The layer that separated was removed, and the remaining liquid was extracted with ether, the extract being added to the liquid already removed. The ether solution was dried with sodium sulfate. After removal of ether, 4.3 g of the oily ethyl (1-aminocyclohexyl)phenylphosphinate was obtained. An ethereal solution of picric acid was added and the picrate was precipitated. Recrystallization from alcohol yielded yellow crystals, m.p. 168°.

Found %: N 2.8; 2.8; P 6.4; 6.3

$C_{20}H_{25}N_4PO_9$. Calculated %: N 2.8; P 6.2

(1-Aminocyclohexyl)phenylphosphinic Acid (XI)

A mixture of 2 g of the hydrochloride of ethyl (1-aminocyclohexyl)phenylphosphinate and 60 ml of 1 : 1 hydrochloric acid was heated in two sealed tubes at 115-125° for three hours. The contents were then evaporated down on a boiling water bath to a residue of constant weight free from the odor of HCl. The solid residue was recrystallized from water, and 2.1 g (75%) of a colorless crystalline substance melting at 212° was obtained. It crystallized with one molecule of water.

Found %: C 56.2; 56.2; H 7.9; 8.0; P 12.3; 12.6; N 5.4; 5.3; $H_2O$ 7.5

$C_{12}H_{18}PNO_2 \cdot H_2O$ (XI). Calculated %: C 56.0; H 7.8; P 12.1; N 5.4; $H_2O$ 7.0

An aqueous solution of the substance was neutral to litmus.

(2-Acetamido-1-methylethyl)phenylphosphinic Acid (XII)

A mixture of 2.9 g of (1-amino-1-methylethyl)phenylphosphinic acid and 8 g of acetic anhydride was heated under reflux in a boiling water bath for 90 minutes. Acetic anhydride was removed under reduced pressure, and the residue - a yellowish glassy mass - solidified when rubbed out with dry ether. Crystallization from alcohol yielded 2.85 g (78%) of a colorless substance, m. p. 197-198°.

Found %: C 54.9; 54.7; H 6.6; 6.7; P 12.8; 12.5; N 5.7; 5.6

$C_{11}H_{16}PNO_3$. Calculated %: C 54.8; H 6.6; P 12.9; N 5.8

Ethyl (1-Hydroxy-1-methylethyl)phenylphosphinate (XIV)

Sodium ethoxide solution (0.4 ml) was added dropwise to a mixture of 17 g of ethyl hydrogen phenylphosphonite and 5.8 g of acetone. The temperature of the mixture rose to 70°. The mixture was heated for 30 minutes in a boiling water bath. On the next day the solid precipitate was filtered off and recrystallized from absolute ethanol.

The product was 5.2 g (23%) of colorless crystals, m.p. 94-96°, readily soluble in water, alcohol, and benzene.

| | | | | |
|---|---|---|---|---|
| | Found %: | C 58.1; 58.0; | H 7.4; 7.6; | P 13.5; 13.7 |
| $C_{11}H_{17}PO_3$. | Calculated %: | C 57.9; | H 7.5; | P 13.6; |

(1-Hydroxy-1-methylethyl)phenylphosphinic Acid (XIII)

A. Reaction of Nitrous Acid with (1-Amino-1-methylethyl)phenylphosphinic Acid. Oxides of nitrogen were passed through a solution, cooled with ice water, of 2 g of (1-amino-1-methylethyl)phenylphosphinic acid in 25 ml of water until nitrogen ceased to be evolved (two hours). Toward the end of the reaction the solution was heated at 40° for 15 minutes. The solution was evaporated down under reduced pressure at 40°. The residue was dried in a vacuum desiccator over caustic alkali and phosphoric oxide. Crystallization from a mixture of chloroform and petroleum ether yielded 0.8 g (40%) of colorless crystals, m.p. 163°.

| | | | | |
|---|---|---|---|---|
| | Found %: | C 54.2; 54.2; | H 6.5; 6.4; | P 15.5 |
| $C_9H_{13}PO_3$. | Calculated %: | C 54.0; | H 6.5; | P 15.5 |

The equivalent weight was determined by titration to phenolphthalein with 0.1 N NaOH. The value obtained was 199 (value calculated, 200).

B. Hydrolysis of Ethyl (1-Hydroxy-1-methylethyl)phenylphosphinate (XIV). A mixture of 2.3 g of ethyl (1-hydroxy-1-methylethyl)phenylphosphinate and 45 ml of 1 : 1 hydrochloric acid was heated in two sealed tubes at 120-125° for three hours. The liquid was evaporated down on a boiling water bath, heating being continued until the odor of hydrogen chloride had disappeared completely, and the residue was recrystallized from benzene. The product was 1 g (50%) of a colorless crystalline substance, m.p. 162-163°.

| | | | | |
|---|---|---|---|---|
| | Found %: | C 54.0; 54.1; | H 6.5; 6.4; | P 15.7; 15.6 |
| $C_9H_{13}PO_3$. | Calculated %: | C 54.0; | H 6.5; | P 15.5; |

The equivalent weight was determined by titration to phenolphthalein with 0.1 N NaOH. The value obtained was 198 (value calculated, 200).

There was no depression in a mixture melting point test with the substance obtained by the action of nitrous acid on (1-amino-1-methylethyl)phenylphosphinic acid.

## SUMMARY

1. The reaction between monoesters of phenylphosphonous acid, ketones or aldehydes, and ammonia has been studied. (1-Amino-1-methylethyl)-, (1-amino-1-methylpropyl)-, (α-aminobenzyl)-, and (1-aminocyclohexyl)-phenylphosphinic acids have been prepared, and also the hydrochlorides of their ethyl esters.

2. With (1-amino-1-methylethyl)phenylphosphinic acid as working example, the structure of the synthesized compounds has been proved. (1-Amino-1-methylethyl)phenylphosphinic acid can be converted in the usual way into its acetyl derivative, and treatment with nitrous acid converts it into the corresponding hydroxy acid.

3. A mechanism has been proposed for the reaction; it is considered that the alkyl hydrogen phenylphosphonite ionizes under the influence of ammonia and its anion then adds to the carbonyl compound; this is followed by replacement of the hydroxy group by amino.

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* T.p. = C. B. Translation pagination

# MECHANISM OF THE FORMATION OF POLYPHENYLPOLYSILOXANES FROM TERFUNCTIONAL "MONOMERS"

K. A. Andrianov and A. A. Zhdanov

Modern methods of preparing organopolysiloxanes are based on the hydrolysis and condensation reactions undergone by bi- and ter-functional alkylhalo- and alkylalkoxy-silanes. In these processes, condensation is generally not separable from hydrolysis, for when these monomeric compounds are treated with water immediate formation occurs of polymeric substances of greater or less degree of polymerization.

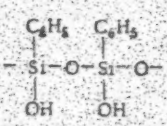
The mechanism of the formation of organopolysiloxanes from bifunctional "monomers" has been the subject of several investigations in which polymer formation has been regarded as a stepwise condensation process [1-6] or as a mixed condensation-polymerization process [7]. Investigations on the reactions of terfunctional monomers have been much fewer.

Data in the literature refer only to the partial hydrolysis of alkyltriethoxysilanes in presence of an insufficient amount of water, i.e., under such conditions that one of the functional groups does not take part in the hydrolysis reaction [8]. There are no definite data in the literature about the structure, and mechanism of formation, of polymers obtained when terfunctional monomers are hydrolyzed with excess of water. Recent work with the object of isolating monomeric substances or primary condensation products in the hydrolysis of terfunctional monomers did not yield positive results [9]. The hydrolysis of dialkyldichlorosilanes results in the formation of a mixture of cyclic and linear polymers. The relative amounts of cyclic and linear molecules in the polymer depend on various conditions and may vary over a wide range. It may be stated as a general rule that increase in the concentration of the acid used for the hydrolysis leads to an increase in the yield of cyclic products.

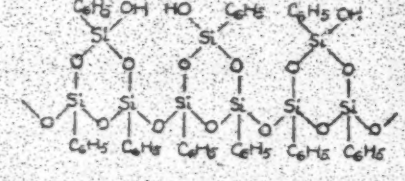
The object of the present investigation was the eludication of the structure of polymers formed from terfunctional monomers by hydrolysis in strongly acid and weakly acid media. With this in view we have hydrolyzed trichlorophenylsilane with various amount of water in presence of diethyl ether as solvent, and we have characterized the resulting polymers by their silicon and hydroxyl contents and by the relative viscosity of a 30% solution of the polymer in toluene. The results are given in the table.

These results are in obvious conflict with usually accepted ideas about the linear or three-dimensional structure of a polymer resulting from the hydrolysis of a terfunctional monomer.

If, in fact, we regard the polymer formed when trichlorophenylsilane is hydrolyzed in an acid medium in presence of solvent as linear, its structure should be:



The repeating unit of such a polymer should contain 20.29% of silicon and 12.71% of hydroxyl groups, and these figures are not in accord with the analytical results. The possibility of formation of cross links between the linear molecules must be excluded, since these polymers of low hydroxyl content are very readily soluble in most organic solvents, including benzene, acetone, diethyl ether, propyl alcohol, butyl alcohol, toluene, and ethyl acetate – they are insoluble only in methanol and ethanol. On the basis of the results obtained we consider that the polymers that we have obtained contain internal rings in their structure, as, for example, in the following scheme:

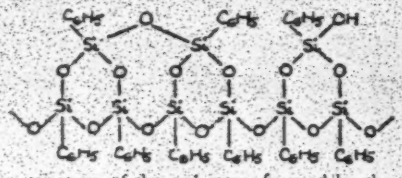


TABLE

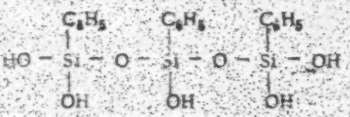
| Expt. No. | Acidity of aqueous layer (%) | Silicon content of polymer(%) | Hydroxyl content of polymer (%) | Time of efflux of a 30% polymer solution (seconds) |
|---|---|---|---|---|
| 1 | 21,2 | 22,61 | 2,20 | 519 |
| 2 | 14.1 | 21,83 | 1,97 | 188 |
| 3 | 9.2 | 22,08 | 2,02 | 143 |
| 4 | 7.9 | 22,63 | 2,38 | 144 |
| 5 | 6.7 | 22,25 | 2,24 | 130 |

The repeating unit of such a polymer should contain 21.23% of silicon and 4.29% of hydroxyl groups, and although these figures are more in accord with the experimental values, they are nevertheless different. In a polymer of this structure, however, further condensation of hydroxyl groups can occur with the formation of more intramolecular oxygen bridges, and without conversion to a polymer of three-dimensional structure. We do not altogether reject the possibility of the occurrence of some intermolecular condensation between hydroxyl groups, but consider this process less probable, because of steric hindrance by the aromatic nucleus attached to the silicon atom. Indirect confirmation of these views is provided by the fact that, in spite of their high functionality, polyphenylpolysiloxane resins, when heated for a long time at 200° behave like thermoplastic polymers.

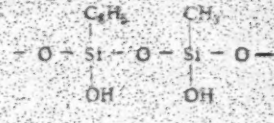
Hence, when terfunctional organosilicon monomers are hydrolyzed in a strongly acid medium in presence of solvent, polymers containing internal rings are formed. The possibility of cross-linking between polymer molecules is directly dependent on the size of the organic radical. With increase in its size and in its steric hindrance effect, intramolecular condensation tends to become predominant. We consider that the organosilicon polymer formed by the hydrolysis of trichlorophenylsilane with water in presence of diethyl ether has the following structure:



We were interested also in the structure of the polymers formed by the hydrolysis of triacetoxyphenylsilane (phenylsilanetriol triacetic ester), since the acid formed is then the weak acetic acid, giving a low hydrogen ion concentration in the aqueous phase. At this low acidity we expected that linear polymers would be formed. As a result of our experiments on the hydrolysis of triacetoxyphenylsilane we isolated the linear trimer 1,3,5-triphenyltrisiloxane-1,1,3,5,5-pentol:



Co-hydrolysis of triacetoxyphenylsilane and triacetoxymethylsilane yielded linear polymers, which, according to the analytical results for silicon and hydroxyl groups, corresponded exactly to the following structure:



These polymers, formed by hydrolysis of triacetoxyalkyl- and triacetoxyaryl-silanes and containing a considerable number of hydroxyl groups, differ qualitatively from the analogous polymers prepared by the hydrolysis of alkyltrichlorosilanes in many of their properties, of which the most characteristic is solubility. They are, for example, highly soluble in ethanol and methanol, and some of them (polymethylpolysiloxanes) are insoluble in benzene, although the products of the hydrolysis of trichloromethylsilane are readily soluble in benzene.

## EXPERIMENTAL

Hydrolysis of Trichlorophenylsilane. A mixture of 50 ml of water and 75 ml of diethyl ether was prepared in a three-necked flask fitted with stirrer, dropping funnel, and thermometer. The mixture was stirred continuously, and a solution of 42.3 g (0.2 mole) of trichlorophenylsilane (b.p. 201°, chlorine content 50.35%) in 75 ml of diethyl ether was added from the dropping funnel over a period of 30 minutes. The reaction temperature was 18-20° during the whole of this time. The mixture was then stirred for a further 30 minutes, after which the organic layer was separated

from the aqueous layer, washed with water until neutral, and dried with sodium sulfate. The solution was filtered, ether was removed under reduced pressure, and the last traces of solvent were removed from the polymer in a vacuum dryer at 40° and a residual pressure of 20 mm until constant weight was attained.

Other experiments on the hydrolysis of trichlorophenylsilane were carried out by the same procedure, the only difference being in the amount of water taken for the hydrolysis of the same amount of trichlorophenylsilane in presence of the same amount of ether. The amounts of water taken in the second, third, fourth, and fifth experiments were 125, 200, 250, and 300 ml respectively. In all of these experiments the products were colorless brittle polymers, soluble in benzene, ether, acetone, and ethyl acetate, but insoluble in ethanol.

The hydroxyl contents of these polymers were determined by the Chugaev-Tserevitinov method. Silicon was determined by wet combustion of a weighed sample with fuming sulfuric acid and calcination of the residue to constant weight. The analytical results are given in the table.

Triacetoxyphenylsilane. Triacetoxyphenylsilane was prepared by a slight modification of the procedure described previously for the preparation of triacetoxymethylsilane (10). A mixture of 211.5 g (1 mole) of trichlorophenylsilane and 306 g (3 moles) of acetic anhydride was allowed to stand at room temperature for 12 hours, and was then heated in a flask fitted with a dephlegmator and condenser set for distillation, it being arranged that the temperature of the vapor passing into the condenser was not higher than 55°.

When 220 g (about 2.8 moles) of acetyl chloride had collected in the receiver, the residue was transferred to a Claisen flask, and unchanged acetic anhydride and trichlorophenylsilane were distilled off up to a temperature of 85° at 8 mm. When cooled, the reaction product solidified to a crystalline mass. This crystalline product, which was later used in hydrolysis experiments, was analyzed for acetyl and silicon content.

| | | |
|---|---|---|
| | Found % | $OCOCH_3$ 62.81; Si 9.80 |
| $C_{12}H_{14}O_5Si$. | Calculated % | $OCOCH_3$ 62.73; Si 9.94 |

Cohydrolysis of Triacetoxyphenylsilane and Triacetoxymethylsilane. A mixture of 70.58 g (0.25 mole) of triacetoxyphenylsilane and 55.05 g (0.25 mole) of triacetoxymethylsilane was prepared in a three-necked flask fitted with stirrer, dropping funnel, and thermometer. The mixture was stirred, and 9 g (0.5 mole) of water was added. The temperature of the reaction mixture then rose to 45°. The mixture was cooled, and 400 ml of ether and 200 ml of water were added to complete the hydrolysis. The mixture was stirred for 30 minutes and the organic layer was then separated, washed until neutral, and dried with sodium sulfate. The solution was filtered, ether was removed at a residual pressure of 25 mm and up to a temperature of 50°, and residual solvent was removed from the polymer in a vacuum dryer at 40° and 20 mm until constant weight was attained. The product was 45 g (53.5%) of a resin, soluble in ethanol, methanol, ether, and acetone.

| | | |
|---|---|---|
| | Found % | Si 26.18; OH 14.33 |
| $C_7H_{10}O_4Si$. | Calculated % | Si 26.16; OH 15.86 |

Hydrolysis of Triacetoxyphenylsilane and Isolation of Crystalline 1,3,5-Triphenyltrisiloxane-1,1,3,5,5-pentol. Water (250 ml), contained in a three-necked flask fitted with stirrer, dropping funnel, and thermometer, was vigorously stirred under cooling to 0° while a solution of 70.58 g (0.25 mole) of triacetoxyphenylsilane in an equal amount of ether was added. When the hydrolysis was complete, the organic layer was separated, washed until neutral, and dried with sodium sulfate. Solvent was removed at 20° and 15 mm residual pressure, and an opaque, greasy residue was obtained. This was treated with 50 ml of benzene, and the insoluble part, which consisted of fine crystals, was filtered off. The crystalline product was washed twice with benzene and dried in a vacuum desiccator. The yield was 4.7 g (12.3%).

| | | |
|---|---|---|
| | Found % | Si 19.45, C 49.31; H 4.89; O 26.31 |
| $C_{18}H_{20}O_7Si_3$. | Calculated % | Si 19.44, C 50.00; H 4.63; O 26.93 |

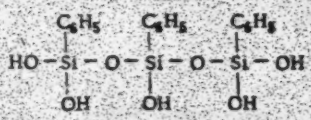
The molecular weight, determined cryoscopically in dioxane, was 433 (calculated value, 432). The substance melted at 113.5-114°, and when it melted, condensation with formation of transparent polymer and separation of water was observed. 1,3,5-Triphenyltrisiloxane-1,1,3,5,5-pentol forms a clear solution in water. When acidified with mineral acids and when heated, its aqueous solution becomes turbid and a precipitate is formed.

## SUMMARY

1. It has been shown that, when terfunctional organosilicon monomers are hydrolyzed in an aqueous medium in presence of mineral acids, complex cyclic polymeric products are formed which do not readily pass, when heated, into three-dimensional polymers, since further condensation occurs by two competing reactions—intramolecular de-

hydration and intermolecular condensation. The first reaction predominates when the organic radical attached to silicon is large, and the second when it is small.

2. Hydrolysis of triacetoxyphenylsilane in a weakly acid medium (acetic acid) yielded the crystalline trimer 1,3,5-triphenyltrisiloxane-1,1,3,5,5-pentol:



3. Hydrolysis of terfunctional monomers in a weakly acid medium (in presence of organic acids) results in the formation of linear polymers. This view is confirmed by the isolation of the crystalline product 1,3,5-triphenyltrisiloxane-1,1,3,5,5-pentol and by the analytical data on the more complex polymers.

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# SYNTHESIS OF SOME ORGANIC DERIVATIVES OF MONO- AND DI-THIONOPYROPHOSPHORIC ACIDS

B. A. Arbuzov, P. I. Alimov, M. A. Zvereva, I. D. Neklesova, and M. A. Kudrina

Investigations of recent years have shown that esters and alkylamides of pyrophosphoric acid and of its sulfur analogs are effective substances for use in combating agricultural pests. Substances that have now been prepared include various esters of pyrophosphoric and dithionopyrophosphoric acid, tetraethyl monothionopyrophosphate, and alkylamides of pyrophosphoric acid [1]. All of these groups of compounds, however, have not only insecticidal activity, but also toxicity to warm-blooded animals. Pyrophosphoric esters are the most toxic, then follow monothionopyrophosphoric esters, and tetraethyl dithionopyrophosphate and the tetrakis(dimethylamide) of pyrophosphoric acid are of relatively low toxicity.

In the present paper we give the results of experiments on preparation of: ethyl esters, mixed alkyl esters and mixed ester-alkylamides of mono- and di-thionopyrophosphoric acids. The object of the work was the preparation of new insecticides of the thionopyrophosphoric acid series.

The method that we used for the synthesis of these organic derivatives of mono- and di-thionopyrophosphoric acids was essentially that used by Toy [2] for the preparation of tetralkyl dithionopyrophosphates. This method consists in the action of the calculated amount of water on a dialkyl phosphorochloridothionate in presence of pyridine or other base:

$$1.\ (AlkO)_2PCl + H_2O + C_5H_5N = (AlkO)_2P(S)OH + C_5H_5N \cdot HCl$$

$$2.\ (AlkO)_2P(S)OH + ClP(OAlk)_2 + C_5H_5N = (AlkO)_2P(S)-O-P(S)(OAlk)_2 + C_5H_5N \cdot HCl.$$

The diethyl hydrogen phosphorothionate that we required for our syntheses was prepared not by the decomposition of its acid chloride by water, as in Toy's method, but by the addition of sulfur to diethyl hydrogen phosphite at 60° in presence of an amine, such as pyridine, triethylamine, or diethylaniline.

$$(C_2H_5O)_2POH + S = (C_2H_5O)_2P(S)OH$$

The resulting diethyl hydrogen phosphorothionate was treated with various acid chlorides of organic derivatives of phosphoric acid, for example

$$(C_2H_5O)_2P(S)OH + ClP[N(CH_3)_2]_2 + (C_2H_5)_3N =$$

$$= (C_2H_5O)_2P(S)-O-P(O)[N(CH_3)_2]_2 + (C_2H_5)_3N \cdot HCl.$$

The known tetraethyl esters of mono- and di-thionopyrophosphoric acids were also prepared by this method.

The insecticidal properties of the synthesized substances were tested on the corn weevil. The weevils were contained in small beakers standing on a rotating disk under a glass bell jar, and they were sprayed with an aqueous solution of the preparation at a definite concentration with the aid of an atomizer and air blower.

The sprayed weevils and the controls were observed over a period of seven days.

Table 1 gives the formulas, physical constants and yields of the compounds, the amines used for binding hydrogen chloride, and the comparative toxicities to the corn weevil under spray conditions. It will be seen from Table 1 that, with respect to the corn weevil, the effectiveness of the mixed alkyl esters and amide-esters of monothionopyrophosphoric acid (No. 2, 3, 4, 5, 6, and 7) is less than that of tetraethyl monothionopyrophosphate (No. 1). The same is true for the amide-esters of dithionopyrophosphoric acid (No. 9 and 10), as compared with tetraethyl dithionopyrophosphate (No. 8). Compounds No. 1, 4, 8, and 9 were tested on warm-blooded animals. The results of these tests are given in Table 2. Table 2 shows that the mixed dimethylamide-esters of mono- and di-thionopyrophosphoric acids (No. 4 and

TABLE 1

| No. | Formula of compound | B.p. in °C (p in mm Hg) | $n_D^{20}$ | $d_4^{20}$ | Phosphorus content (%) Found | Phosphorus content (%) Calculated | Yield (%) | Amine | Toxicity to the corn weevil (by spray) Concentration (%) | Toxicity to the corn weevil (by spray) Proportion killed after 7 days (%) |
|---|---|---|---|---|---|---|---|---|---|---|
| 1 | $(C_2H_5O)_2P(O)-O-P(OC_2H_5)_2$ (O, S) | 127.5–128.5(1) | 1.4523 | 1.1930 | 20.56<br>20.31 | 20.56 | 72.4<br>68.3<br>66.2 | Triethylamine<br>pyridine<br>diethylaniline | 0.005 | 100 |
| 2 | $(i\text{-}C_3H_7O)_2P(O)-O-P(OC_2H_5)_2$ (O, S) | 125–126 (2) | 1.4439 | 1.1322 | 18.91<br>18.88 | 18.56 | 52.3 | Triethylamine | 0.05 | 75 |
| 3 | $(C_2H_5O)_2P(O)-O-P(OC_2H_5)_2$ (O, S) | 147–149(2) | 1.4512 | 1.1161 | 17.24<br>17.38 | 17.12 | 30.1 | Triethylamine | 0.05 | 100 |
| 4 | $(CH_3)_2N$, $C_2H_5O$ on P(O)–O–P(OC$_2$H$_5$)$_2$ (O, S) | 120 (1) | 1.4593 | 1.1784 | 20.46<br>20.55 | 20.32 | 68.6 | Triethylamine | 0.05 | 100 |
| 5 | $(C_2H_5)_2N$, $C_2H_5O$ on P(O)–O–P(OC$_2$H$_5$)$_2$ (O, S) | 143–145 (1) | 1.4595 | 1.1402 | 18.38<br>18.58 | 18.65 | 17.6 | Triethylamine | 0.05 | 75 |
| 6 | $[(CH_3)_2N]_2P(O)-O-P(OC_2H_5)_2$ (O, S) | 127–128 (1) | 1.4719 | 1.1667 | 20.46<br>20.62<br>S<br>10.54<br>10.51 | 20.59<br>S<br>10.52 | 42.4 | Triethylamine | 0.1 | 60 |
| 7 | $[(C_2H_5)_2N]_2P(O)-O-P(OC_2H_5)_2$ (O, S) | 163–166(2) | 1.4669 | 1.0871 | 16.95<br>16.87 | 17.22 | 13.1 | – | – | – |
| 8 | $(C_2H_5O)_2P(S)-O-P(OC_2H_5)_2$ (S, S) | 134–135(2.5) | 1.4775 | 1.1897 | – | – | 62.7 | Triethylamine | 0.05 | 100 |
| 9 | $(CH_3)_2N$, $C_2H_5O$ on P(S)–O–P(OC$_2$H$_5$)$_2$ (S, S) | 135 (2) | 1.4821 | 1.1829 | 19.17<br>19.24 | 19.31 | 53.5 | Triethylamine | 0.05 | 70 |
| 10 | $[(C_2H_5)_2N]_2P(S)-O-P(OC_2H_5)_2$ (S, S) | 168.5–170 (3) | – | – | 16.3<br>16.23<br>S16.79<br>16.64 | 16.48<br>S17.02 | 38.5 | – | 0.1 | 45 |

and diethylaniline) than tetraethyl mono- and di-thionopyrophosphates (Nos. 1 and 8) respectively. It will be noted that preparation No. 6 is less effective than preparation No. 8 when applied to the corn weevil, but the difference is not significant, for the toxicity of No. 9 to warm-blooded animals is much less than that of No. 8 (replacement of amine by dimethylaniline).

1. Preparation of Diethyl Hydrogen Phosphorothionate

A mixture of 18 g (one molecular proportion) of diethyl hydrogen phosphite and 13.2 g (one molecular proportion) of triethylamine was stirred while 4.17 g (one atomic proportion) of sulfur powder was added in portions. The sulfur reacted vigorously with the diethyl hydrogen phosphite and, owing to the evolution of heat, it was necessary to cool the reaction flask with water every now and then. The mixture was then heated for 10–15 minutes at 50° and all of the sulfur went into solution.

The addition of sulfur to diethyl hydrogen phosphite is less vigorous in presence of pyridine or diethylaniline. When these amines were used, the sulfur was add gradually to a mixture of diethyl hydrogen phosphite and amine at 50–55°, and the mixture was then stirred at 60° for 60–90 minutes.

2. Preparation of Derivatives of Mono- and Di-thionopyrophosphoric Acids

The calculated amount of the acid chloride of an organic derivative of phosphonic acid was added at 30–35°

to diethyl hydrogen phosphorothionate, prepared as in the first experiment, containing dissolved amine (triethylamine, pyridine or diethylaniline); the hydrochloride of the amine separated out.

The thick mass was stirred for 2-3 hours at 35-40°, cooled, and diluted with gasoline (b.p. 75-125°). The precipitate was filtered off. The gasoline was removed under reduced pressure, and the residue was vacuum-distilled.

In this way compounds No. 1, 2, 3, 4, 5, 6, 8, and 9 (Table 1) were prepared. Compounds No. 7 and 10 were prepared by reaction of the corresponding acid chlorides with sodium diethyl phosphorothionate.

TABLE 2

Toxicity of Preparations to White Mice and Guinea Pigs

| Compound | White mice (subcutaneously) | | Guinea pigs | |
|---|---|---|---|---|
| | LD50 (mg/kg) | LD100 (mg/kg) | LD50 (mg/kg) | LD100 (mg/kg) |
| $(C_2H_5O)_2P(O)-O-P(S)(OC_2H_5)_2$ (1) | – | 0.25 | 4 | 6 |
| $(CH_3)_2N-P(O)(OC_2H_5)-O-P(S)(OC_2H_5)_2$ (4) | 2 | – | 7 | 10 |
| $(C_2H_5O)_2P(S)-O-P(S)(OC_2H_5)_2$ (8) | – | 8 | 15 | 40 |
| $(CH_3)_2N-P(S)(OC_2H_5)-O-P(S)(OC_2H_5)_2$ (9) | 30 | 40 | 40 | 60 |


## SUMMARY

1. Diethyl hydrogen phosphorothionate has been prepared by the addition of sulfur to diethyl hydrogen phosphite in presence of one of the following amines: triethylamine, pyridine, and diethylaniline.

2. Ethyl esters, some mixed alkyl esters, and some mixed ester-amides of mono- and di-thionopyrophosphoric acids have been synthesized.

3. Tests have been made of the action of the synthesized substances on the corn weevil, and four of them have been tested on white mice and guinea pigs.


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# SYNTHESIS OF SOME N-SUBSTITUTED DERIVATIVES OF DIETHYL PHOSPHORAMIDATE

B. A. Arbuzov, P. I. Alimov, and M. A. Zvereva

Many organic compounds of phosphorus and nitrogen containing a phosphorus-nitrogen bond (P–N) are known. They are readily prepared, for example by the action of ammonia or an amine on the acid chloride of an organic derivative of a phosphorus acid. In compounds obtained in this way, the hydrogens on the nitrogen can be replaced by various alkyl and aryl radicals.

Amides are known in which one of these hydrogens is replaced by acyl. Such compounds have been prepared in very low yield by the action of phosphorus pentachloride on chloro- or bromo-acetamides [1] and by the action of N-bromoamides of carboxylic acids on sodium dialkyl phosphites [2].

In the present paper we describe two methods for the preparation of diethyl phosphoramidates and phosphoramidites in which various acid residues are attached to nitrogen. One of these methods consists in the action of tetraethyl pyrophosphite on a carboxamide:

$$CH_3CONH_2 + (C_2H_5O)_2P-O-P(OC_2H_5)_2 = CH_3\cdot CONHP(OC_2H_5)_2 + HOP(OC_2H_5)_2$$

and the second method – in the action of acid chlorides of organic and mineral acids, and also of alkyl halides, on N-sodium derivatives of diethyl N-alkylphosphoramidates.

When diethyl N-monoalkyl- and N-monoaryl-phosphoramidates are treated with sodium, sodium derivatives are formed which are readily soluble in organic solvents:

$$(C_2H_5O)_2\underset{\underset{O}{|}}{P}-\underset{\underset{CH_3}{|}}{NH} + Na = (C_2H_5O)_2\underset{\underset{O}{||}}{P}-\underset{\underset{CH_3}{|}}{N}Na + H$$

When the latter compounds are treated with halogen-containing compounds, various amide derivatives can be obtained, for example:

$$C_2H_5OCOCl + \underset{\underset{CH_3}{|}}{NaN}-\underset{\underset{O}{||}}{P}(OC_2H_5)_2 = NaCl + C_2H_5OCON\underset{\underset{CH_3}{|}}{}-\underset{\underset{O}{||}}{P}(OC_2H_5)_2$$

Similarly, phosgene and diethyl N-methyl-N-sodiophosphoramidate yielded an organophosphorus urea derivative:

$$COCl_2 + 2NaN\underset{\underset{CH_3}{|}}{}-\underset{\underset{O}{||}}{P}(OC_2H_5)_2 = 2NaCl + (C_2H_5O)_2\underset{\underset{O}{||}}{P}-\underset{\underset{CH_3}{|}}{N}-CO-\underset{\underset{CH_3}{|}}{N}-\underset{\underset{O}{||}}{P}(OC_2H_5)_2$$

In this way, by the action of diethyl N-methyl-N-sodiophosphoramidate on ethyl chloroformate, diethylcarbamoyl chloride, phosgene, ethyl phosphorodichloridite, sulfur dichloride, methylene dibromide, and ethyl bromoacetate, the corresponding derivatives of diethyl phosphoramidate were obtained. The formulas of these compounds, and their physical constants and yields are given in the table. All the substances in the table are colorless liquids; some of them are mobile, others are more viscous. They are soluble in water and organic solvents. Tests on corn weevils showed that these compounds are not insecticides.

## EXPERIMENTAL

### 1. Action of Tetraethyl Pyrophosphite on Acetamide

Acetamide (2.8 g) was added to 12.2 g of tetraethyl pyrophosphite contained in an Arbuzov distillation flask, and the mixture was heated for 15 minutes at a bath temperature of 120°. As a result of several distillations, two main fractions were obtained. Fraction I, b.p. 70–71° at 10 mm, $n_D^{20}$ 1.4085; $d_4^{20}$ 1.0713, was diethyl hydrogen phosphite (one of the reaction products); the yield was 5 g (76.5%). Fraction II, b.p. 88.5–89.5° at 3 mm, was obtained in 40.4% yield (3.4 g); it had $n_D^{20}$ 1.4375.

$C_6H_{14}PO_3N$. Found %: P 17.36; 17.11
Calculated %: P 17.31

The substance is a colorless liquid smelling of acetamide. It is soluble in water and organic solvents.

2. Action of Ethyl Chloroformate on Diethyl N-Methyl-N-sodiophosphoramidate

Preparation of Diethyl N-Methyl-N-sodiophosphoramidate Required in This and Subsequent Preparations. The reaction was carried out in a flask fitted with stirrer, reflux condenser, and dropping funnel. Gasoline (b.p. 75-125°) was poured into the flask, the volume taken being 6-6.5 times as great as the volume of the diethyl N-methylphosphoramidate to be taken for reaction. A certain excess of sodium was added in the form of lumps and the ester-amide was added dropwise at room temperature. Reaction was vigorous. The sodium derivative of the amide remained in solution. When the addition was complete, the flask was heated in a bath at 60-70° for 1.5-2 hours. When reaction was complete, as indicated by the cessation of evolution of hydrogen bubbles, the excess of sodium was removed. The amount of sodium that reacted was exactly the amount calculated.

Reaction with Ethyl Chloroformate. Ethyl chloroformate (10 g) was added from a dropping funnel to a water-cooled gasoline solution of diethyl N-methyl-N-sodiophosphoramidate prepared from 15.5 g of the amide and 2.13 g of sodium. Sodium chloride separated immediately. In order to complete the reaction, the reaction mixture was heated in a bath at 80-70° for 30-40 minutes. The mixture was cooled, the sodium chloride was centrifuged off, and the gasoline was distilled off under somewhat reduced pressure.

The residue of 18.2 g (82.3%) was fractionated. Two fractionations from an Arbuzov flask yielded 12 g (54.3%) of a substance boiling at 95-96° (1.5 mm) and having $n_D^{20}$ 1.4299; $d_4^{20}$ 1.1311.

Found % P 13.17; 13.04

$C_8H_{18}PO_5N$. Calculated % P 12.97

The substance is a colorless odorless mobile liquid, readily soluble in water and organic solvents.

TABLE

| Formula of compound | B.p. in °C (p in mm Hg) | $n_D^{20}$ | $d_4^{20}$ | Yield (%) |
|---|---|---|---|---|
| $CH_3CONHP(OC_2H_5)_2$ | 88.5–89.5 (3) | 1.4375 | – | 40.4 |
| $C_2H_5OCON-PO(OC_2H_5)_2$ (CH3) | 95 – 95 (1.5) | 1.4299 | 1.1311 | 54.3 |
| $C_6H_5N(CH_3)CON-PO(OC_2H_5)_2$ (CH3) | 112 (1) | 1.4478 | 1.0849 | 46.1 |
| $(C_2H_5O)_2P(O)-N(CH_3)-CO-N(CH_3)-P(O)(OC_2H_5)_2$ | 145–146.5 (0.5) | 1.4505 | 1.2019 | 21.9 |
| $C_6H_5OPCl-PO(OC_2H_5)_2$ (CH3) | 170 (0.5) | 1.4562 | 1.1725 | 19.6 |
| $C_6H_5O(O)P-N(CH_3)-S-N(CH_3)-P(O)(OC_2H_5)_2$ | 161–163 (2) | 1.4800 | 1.1908 | 37.8 |
| $(C_2H_5O)_2P(O)-N(CH_3)-CH_2-N(CH_3)-P(O)(OC_2H_5)_2$ | 149–150 (1) | 1.4394 | 1.1309 | 11.5 |
| $CH_3OCOCH_2NPO(OC_2H_5)_2$ (CH3) | 112–114 (2) | 1.4295 | 1.1048 | 34 |
| $C_2H_5OCOCH_2NHP(O)(OC_2H_5)_2$ (CH3) | 135.5 (1) | 1.4390 | 1.1495 | 74 |

3. Action of Diethylcarbamoyl Chloride on Diethyl N-Methyl-N-sodiophosphoramidate

The acid chloride (8 g) was added to a gasoline solution of sodioamide prepared from 9.86 g of diethyl N-methylphosphoramidate and 1.38 g of sodium. The yield of crude product was 13.1 g (81.2%), and after three distillations 7.5 g (46.1%) of a substance boiling at 112-113° (1 mm) was obtained. It had $n_D^{20}$ 1.4478; $d_4^{20}$ 1.0849.

Found % P 11.86; 11.74

$C_{10}H_{23}PO_4N_2$ Calculated % P 11.65

The substance is a colorless, odorless mobile liquid, soluble in water.

4. Action of Phosgene on Diethyl N-Methyl-N-Sodiophosphoramidate

A solution of 2.4 g of phosgene in 12 ml of toluene was added to a gasoline solution of diethyl N-methyl N-

sodiophosphoramidate prepared from 17.4 g of amide and 2.4 g of sodium. The yield of crude product, a mobile yellow liquid, was 15 g (82%). Distillation yielded Fraction I (3.9 g), b.p. 90-145° (1 mm) and Fraction II (8.5 g), b.p. 145-160° (1 mm).

Fraction II yielded 4.1 g (21.9%) of a substance boiling at 145-146.5° (0.5 mm) and having $n_D^{20}$ 1.4505 and $d_4^{20}$ 1.2019.

Found %: P 17.31; 17.07
$C_{11}H_{26}P_2O_7N_2$. Calculated %: P 17.22

The substance is a colorless, odorless viscous liquid, readily soluble in water and organic solvents.

5. Action of Ethyl Phosphorodichloridite on Diethyl N-Methyl-N-sodiophosphoramidate

The substances taken for reaction were 6.6 g of diethyl phosphorodichloridite, 15 g of diethyl N-methylphosphoramidate, and 2.06 g of sodium. The yield of crude product was 14.9 g (81.4%). Two distillations from an Arbuzov flask yielded 3.6 g (19.6%) of pure product boiling at 170° (1 mm); it had $n_D^{20}$ 1.4569; and $d_4^{20}$ 1.1725.

Found %: P 22.63; 22.75
$C_{12}H_{25}O_7P_3N_2$. Calculated %: P 22.79

The substance is a fairly mobile, colorless, odorless liquid, soluble in water and organic solvents.

6. Action of Sulfur Dichloride on Diethyl N-Methyl-N-sodiophosphoramidate

The substances taken for reaction were 15 g of diethyl N-methylphosphoramidate, 2.34 g of sodium, and 5.23 g of sulfur dichloride. The yield of crude product (a dark-red liquid) was 15.1 g (81.5%).

The first fractionation from an Arbuzov flask yielded:

Fraction I, b.p. 96-160°: 3 g
Fraction II b.p. 160-172°: 10 g

Fraction II yielded 7 g (37.8%) of a substance boiling at 161-163° (2 mm) and having $n_D^{20}$ 1.4600; $d_4^{20}$ 1.1908.

Found %: P 16.62; 16.74
$C_{16}H_{36}O_6P_2SN_2$. Calculated %: P 17.03

The substance is a fairly mobile odorless, yellow liquid, soluble in organic solvents and in water.

7. Action of Methylene Dibromide on Diethyl N-Methyl-N-sodiophosphoramidate

Methylene dibromide (9.16 g) was added to a gasoline solution of diethyl N-methyl-N-sodiophosphoramidate prepared from 17.6 g of amide and 2.42 g of sodium. Reaction began at a bath temperature of about 70°. The reaction mixture was heated at a bath temperature of 85-95° with mechanical stirring for 90 minutes. The yield of crude product (a mobile yellow liquid) was 13 g (71.4%).

The first fractionation from an Arbuzov flask yielded:

Fraction 1, b.p. 60-120° (2 mm): 4.1 g
Fraction 2, b.p. 120-150° (1 mm): 6 g
Residue: 1.5 g

Fraction I was distilled, but no pure substance was isolated. Distillation of Fraction II yielded 2.1 g (11.5%) of a substance boiling at 140-150° (1 mm) and having $n_D^{20}$ 1.4394, $d_4^{20}$ 1.1309.

Analysis of Fraction II, b.p. 140-150° (1 mm):

Found %: P 18.01; 17.78
$C_{11}H_{28}O_6P_2N_2$. Calculated %: P 17.91

The substance is a colorless, odorless, mobile liquid.

8. Action of Ethyl Bromoacetate on Diethyl N-Methyl-N-sodiophosphoramidate

The substances taken for reaction were 15.36 g of ethyl bromoacetate, 15 g of diethyl N-methylphosphoramidate, 2.2 g of sodium, and gasoline as solvent. After the ethyl bromoacetate had been added to the sodioamide, the reaction mixture was kept at room temperature for one hour and at 60-80° in a bath for 30 minutes. The yield of crude product (a dark brown liquid) was 18.5 g (81.5%).

The first distillation (at 2 mm) yielded:

Fraction I, b.p. 108°; 2.2 g
Fraction II, b.p. 108-115°; 11.5 g
Residue 4 g

Distillation of Fraction II yielded 7.7 g (34%) of a substance boiling at 112-114° (2 mm) and having $n_D^{20}$ 1.4295; $d_4^{20}$ 1.1048.

Found %: P 12.26; 12.47
$C_5H_{20}O_5PN$. Calculated %: P 12.25

The substance is a colorless, odorless liquid soluble in water.

## 2. Action of Diethyl Phosphorochloridate on the Ethyl Ester of Glycine

One molecular proportion (17.58 g) of diethyl phosphorochloridate was added to 21.7 g (2.07 molecular proportions) of glycine ethyl ester in ether solution. The mixture was stirred for one hour at room temperature, and the precipitate of the hydrochloride of glycine ester was filtered off and washed with ether. The residue after removal of solvent was 26.6 g.

Two distillations from an Arbuzov flask yielded 18 g (74%) of a product boiling at 135.5° (1 mm) and having $n_D^{20}$ 1.4390; $d_4^{20}$ 1.1495.

Found %: P 13.15; 13.16
$C_6H_{18}O_5PN$. Calculated %: P 12.97

The substance is a colorless, odorless, viscous liquid, soluble in water and organic solvents.

## SUMMARY

Some N-substituted derivatives of diethyl phosphoramidate are described. They were prepared by the action of various halogen compounds on the N-sodium derivative of diethyl N-methylphosphoramidate.

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# SYNTHESIS OF AMIDES OF ORGANIC DERIVATIVES OF PHOSPHORIC ACID

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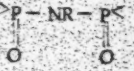
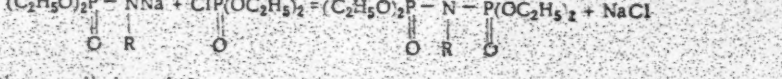
Studies of the insecticidal properties of organic derivatives of pyrophosphoric acid and its sulfur analogs have shown that compounds of this type are very effective for use against many agricultural pests [1]. In these compounds, which are of the anhydride type, two phosphorus atoms are linked through oxygen or sulfur:

We considered that it would be interesting to synthesize similar compounds in which two phosphorus atoms would be linked through nitrogen.



and to investigate their insecticidal properties.

Compounds of this type can be prepared by the action of acid chlorides of organic derivatives of phosphoric, phosphorothionic, and other acids on N-sodium derivatives of diethyl N-alkylphosphoramidates, for example:



When diethyl N-monoalkyl- and N-monoaryl-phosphoramidates are treated with sodium, they readily yield sodium derivatives that are very soluble in organic solvents. In our experiments we used gasoline (b.p. 75-125°, or on one occasion benzene, as solvent. By the reaction referred to above we have prepared several substances of the required type.

The synthesized substances were tested for insecticidal effect on corn weevils. These tests were carried out as follows. Small beakers containing corn weevils were placed on a rotating disk situated under a glass bell jar, and the weevils were then sprayed, by the aid of an air blower and atomizer, with an aqueous solution of the preparation at a definite concentration. Observations were made on the sprayed weevils and on the controls for a period of seven days. The formulas of the compounds and their physical constants, yields, and comparative toxicity for the corn weevil are given in the table. For purposes of comparison, the table gives the result of the same toxicity test for tetraethyl monothionopyrophosphate (No. 10), which is a well known and very effective insecticide, but is unsuitable for extensive use owing to its high toxicity to warm-blooded animals.

The substances described in the table are colorless mobile liquids, soluble in water and organic solvents. As indicated in the table, the substances that we have prepared are lower in insecticidal power than tetraethyl monothionopyrophosphate (No. 10). The most effective was No. 8, the tetraethyl ester of bis[phosphoric acid] butylamide. In aqueous solution at a concentration of 0.05% it killed all the weevils in four hours, at 0.1% – in two hours. This preparation was not obtained in the pure state, and the technical product was used in the test. It is possible that its high insecticidal power, as compared with other compounds of the same type, was derived not from the substance itself, but from impurities. Preparation No. 5 – the tetraethyl ester of the mixed methylamide of phosphoric and phosphorothionic acids – had a very low toxicity.

## EXPERIMENTAL

### Preparation of Diethyl N-Alkyl- N-sodiophosphoramidates

The reaction was carried out in a flask fitted with stirrer, reflux condenser, and dropping funnel. Gasoline (b.p. 75-125°) was poured into the flask, the volume taken being 6-6.5 times as great as the volume of the amide to be taken for reaction. A certain excess of sodium was added in the form of lumps, and the diethyl N-alkylphosphoramidate added dropwise from the funnel. Reaction set in immediately at room temperature. When the addition

of amide was complete, the flask was heated in a water bath for 1.5-2 hours. When reaction was complete, the solution of the alkylsodioamide was cooled, and the excess of sodium was removed. Exactly the calculated amount of sodium reacted.

TABLE

| No. | Formula of compound | B.p. in °C (p in mm Hg) | $n_D^{20}$ | $d_4^{20}$ | Yield (%) | Toxicity to the corn weevil (by spray) | |
|---|---|---|---|---|---|---|---|
| | | | | | | Concentration (%) | Proportion killed after 7 days |
| 1 | $(C_2H_5O)_2P(O)-N(CH_3)-P(OC_2H_5)_2$ | 138–139 (3) | 1.4353 | 1.1666 | 46.3 | 0.05 | 90 |
| 2 | $(C_2H_5O)_2P(O)-N(CH_3)-P[N(CH_3)_2]_2$ | 147–149 (3) | 1.4621 | 1.0432 | 35 | 0.1 | 85 |
| 3 | $(C_2H_5O)_2P(O)-N(CH_3)-P(OC_2H_5)_2$ | 104–106 (1) | 1.4435 | 1.1945 | 43.4 | 0.1<br>0.2 | 60<br>90 |
| 4 | $(C_2H_5O)_2P(O)-N(CH_3)-P(N(CH_3)_2)(OC_2H_5)$ | 139–141 (1.5) | 1.4453 | 1.3831 | 62 | 0.2 | 80 |
| 5 | $(C_2H_5O)_2P(O)-N(CH_3)-P(OC_2H_5)_2$ | 120 (1) | 1.4656 | 1.0420 | 36.5 | 0.1 | 25 |
| 6 | $(C_2H_5O)_2P(O)-N(C_2H_5)-P(OC_2H_5)_2$ | 123–124 (1) | 1.4359 | 1.1468 | 52.15 | 0.1<br>0.2 | 80<br>100 |
| 7 | $(C_2H_5O)_2P(O)-N(C_2H_5)-P[N(CH_3)_2]_2$ | 138–139 (2) | 1.4569 | 1.1345 | 50.9 | 0.1<br>0.2 | 60<br>100 |
| 8 | $(C_2H_5O)_2P(O)-N(C_4H_9)-P(OC_2H_5)_2$ | Technical product | – | – | – | 0.01<br>0.05<br>0.1 | 80<br>100<br>100 |
| 9 | $(C_2H_5O)_2P(O)-N(C_4H_9)-P(OC_2H_5)_2$ | Technical product | – | – | – | 0.1 | 60 |
| 10 | $(C_2H_5O)_2P(S)-O-P(OC_2H_5)_2$ | 127.5–128.5 (1) | 1.4523 | 1.1930 | – | 0.005 | 100 |

1. [Tetraethyl Ester of Bis[phosphoric acid] Methylamide $(C_2H_5O)_2P(O)-N(CH_3)-P(OC_2H_5)_2$

Diethyl phosphorochloridate was added to a stirred water-cooled solution of diethyl N-methyl-N-sodiophosphoramidate (prepared from 15 g of the amide and 2.1 g of sodium) in gasoline. The acid chloride was added over a period of 2½ minutes, and the mixture was then stirred for some time at room temperature and for 20–30 minutes at a bath temperature of 70°. Sodium chloride was removed by centrifugation, solvent was distilled off under reduced pressure, and the remaining 23.5 g (86.3%) of liquid was distilled. Two distillations from an Arbuzov flask yielded 12.6 g (46.3%) of a pure fraction boiling at 138–139° (1 mm) and having $n_D^{20}$ 1.4353; $d_4^{20}$ 1.1666.

Found %: P 20.7, 20.71

$C_9H_{23}P_2NO_5$. Calculated %: P 20.46

The substance is a very mobile, colorless, odorless liquid, soluble in water and ether.

2. Diethyl Ester of the Mixed Methylamide of Phosphoric and N, N, N', N'-Tetramethylphosphorodiamidic Acids $(C_2H_5O)_2P(O)-N(CH_3)-P[N(CH_3)_2]_2$

The compound was prepared by the action of 15 g of N, N, N', N'-tetramethylphosphorodiamidic chloride on diethyl N-methyl-N-sodiophosphoramidate prepared in gasoline solution from 14.7 g of the amide and 2.02 g of sodium. The crude product, amounting to 22.2 g (83.7%), was distilled at a residual pressure of 2.5 mm from an Arbuzov flask, and yielded the fractions:

Fraction I, b.p. 111-142°; 4 g
Fraction II, b.p. 142-144°; 1.3 g
Fraction III, b.p. 144-142°; 12.9 g
Residue 2 g

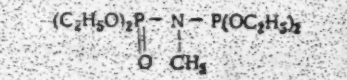
Distillation of Fraction III yielded 9.3 g (35%) of a substance boiling at 147-149° (3 mm) and having $n_D^{20}$ 1.4621; $d_4^{20}$ 1.0452.

Analysis of the fraction boiling at 147-149° (3 mm):

Found %: P 20.95; 20.87
$C_9H_{25}P_2N_3O_4$. Calculated %: P 20.59

The substance is a very mobile, colorless liquid, readily soluble in water and gasoline.

3. Tetraethyl Ester of the Mixed Methylamide of Phosphoric and Phosphorous Acids



The substances taken for reaction were 15 g of diethyl N-methylphosphoramidate, 2.1 g of sodium, and 14.1 g of diethyl phosphorochloridite. The reaction was carried out in gasoline. The yield of crude product, a dark-yellow liquid, was 22.2 g (86%). The first fractionation from an Arbuzov flask at 2 mm yielded:

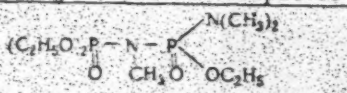
Fraction I, b.p. 42-110°; 2 g
FractionII, b.p. 110-117°; 17.5 g
Residue 2 g

Distillation of Fraction II (17.5 g) yielded 11.2 g (43.4%) of pure product; b.p. 104-106° (1 mm); $n_D^{20}$ 1.4435; $d_4^{20}$ 1.1045.

Found %: P 21.36; 21.35
$C_9H_{23}P_2NO_5$. Calculated %: P 21.6

The substance is a very mobile, colorless liquid having a feeble odor of a phosphorous ester. It is soluble in water.

4. Triethyl Ester of the Mixed Methylamide of Phosphoric and N,N-Dimethylphosphoramidic Acids.

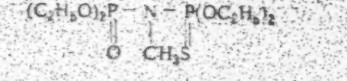


This was prepared similarly to the preceding compound from 15.6 g of diethyl N-methylphosphoramidate, 2.15 g of sodium, and 16.1 g of ethyl N,N-dimethylphosphoramidochloridate. The yield of crude product was 24.1 g (85.4%). Two distillations yielded 17.5 g (62.%) of a fraction boiling at 139-141° and having $n_D^{20}$ 1.4453; $d_4^{20}$ 1.3831.

Found %: P 20.51; 20.46
$C_9H_{24}P_2N_3O_5$. Calculated %: P 20.52

The substance is a very mobile colorless liquid, soluble in water and ether, but not readily soluble in gasoline.

5. Tetraethyl Ester of the Mixed Methylamide of Phosphoric and Phosphorothionic Acids



The substances taken for reaction were diethyl phosphorochloridothionate (13 g), diethyl N-methylphosphoramidate (11.5 g), and sodium (1.58 g). The conditions were as in the preceding experiments. The yield of crude product, a dark-yellow liquid, was 19 g (86.7%). The first fractionation (1.5 mm) yielded:

Fraction I, b.p. 64-110°, 3.6 g
FractionII, b.p. 110-135°; 10.8 g
Residue 3 g

Distillation of Fraction II yielded 8 g (36.5%) of a substance boiling at 120° (1 mm) and having $n_D^{20}$ 1.4656; $d_4^{20}$ 1.0420.

Found %: P 19.42; 19.34
$C_9H_{23}P_2NSO_5$. Calculated %: P 19.43

The substance is a mobile yellow liquid, only slightly soluble in water, but readily soluble in organic solvents.

6. Tetraethyl Ester of Bis[phosphoric acid] Ethylamide $(C_2H_5O)_2P(O)-N(C_2H_5)-P(O)[N(CH_3)_2]_2$

The conditions were as in the preceding experiments. The substances taken were diethyl N-ethylphosphoramidate (15 g), sodium (1.9 g), and diethyl phosphorochloridate (14.3 g). The yield of crude product, a dark-yellow liquid, was 22.6 g (86%). Two distillations yielded 13.7 g (52.15%) of a substance boiling at 123-124° (1 mm).

Found %: P 19.94; 19.96

$C_{10}H_{25}P_2NO_5$. Calculated %: P 19.56

The substance is a very mobile, colorless liquid, readily soluble in water.

7. Diethyl Ester of the Mixed Ethylamide of Phosphoric and N,N,N',N'-Tetramethylphosphorodiamidic Acids $(C_2H_5O)_2P(O)-N(C_2H_5)-P(O)[N(CH_3)_2]_2$

The substance taken for reaction were diethyl N-ethylphosphoramidate (15 g), sodium (1.9 g), and N,N,N',N'-tetramethylphosphorodiamidic chloride (14.12 g). The yield of crude product was 23.1 g (83.5%). Two distillations yielded 13.3 g (50.9%) of a fraction boiling at 138-139° (2 mm) and having $n_D^{20}$ 1.4609; $d_4^{20}$ 1.1345.

Found %: P 19.94; 20.04

$C_{10}H_{27}P_2N_3O_4$. Calculated %: P 19.68

The substance is a fairly mobile, colorless liquid, readily soluble in water and ether.

8. Tetraethyl Ester of Bis[phosphoric acid]Anilide $(C_2H_5O)_2P(O)-N(C_6H_5)-P(O)(OC_2H_5)_2$

Diethyl phosphorochloridate (15.1 g) was added at room temperature to a benzene solution of diethyl N-phenyl-N-sodiophosphoramidate prepared from 20 g of the amide and 2 g of sodium. Reaction was completed by heating the flask in a water bath for one hour. The benzene solution of the product was treated with water to remove sodium chloride and then dried with calcium chloride. The solvent was removed under reduced pressure, and the residue was a fairly mobile, dark-red liquid. The liquid did not crystallize when allowed to stand, and it decomposed when distilled.

## SUMMARY

1. A series of organophosphorus compounds of formula $(C_2H_5O)_2P(O)-NR-PR'_2$ (R is $CH_3$, $C_2H_5$, $C_4H_9$, R' is $N(CH_3)_2$) has been prepared and some of the properties of the compounds have been described.

2. Tests on corn weevils show that compounds of this type are insecticides.

## LITERATURE CITED

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# DETERMINATION OF THE INDIVIDUAL HYDROCARBON COMPOSITION OF GASOLINES BY THE COMBINATION METHOD

## COMMUNICATION 6. KARACHUKHURSK GASOLINE

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In the present communication we give the results of an investigation of the individual hydrocarbon composition of a gasoline having an upper boiling limit of 150° obtained from low-sulfur lower-level Karachukhursk petroleum. The investigation was carried out by the previously described combination method [1], which we have applied to the investigation of two gasolines from Kazanbulak petroleums [2], two Surakhan gasolines [3], a gasoline derived from Tuimazin petroleum [4], and a gasoline from Embensk petroleum [5]. The gasoline used in the present work, like the Surakhan gasolines, was not separated from the petroleum by distillation in the laboratory, but was obtained in the prepared state from the V. V. Kuibyshev Azerbaidzhan Research Institute for the Petroleum-refining Industry.

As a result of the investigation the composition of the Karachukhursk gasoline was accounted for quantitatively to the extent of 85.4%. Altogether, 64 hydrocarbons were found in the gasoline, and the contents of these were determined quantitatively. Their distribution by classes is shown in Table 1.

TABLE 1

Distribution by Classes of the Hydrocarbons Found

| Class of hydrocarbons | Number of hydrocarbons in the gasoline |
|---|---|
| Paraffins | 32 |
| Cyclopentanes | 12 |
| Cyclohexanes | 14 |
| Aromatics | 6 |
| | 64 |

In the further discussion the gasoline under investigation will be denoted by TsCh-1. The same symbols will be used for the fractions as were used in the previous papers [1 - 5].

The contents of all individual hydrocarbons found in the gasoline have been calculated as per cent by weight of the whole gasoline, i.e. all that distils up to 150°, and these figures are given in Table 2. In the same table we give the overall quantitative balance sheet for the investigation, and also the group composition of the Karachukhursk gasoline, in which normal and branched paraffins, and also cyclopentane and cyclohexane hydrocarbons, are considered separately.

As will be seen from Table 2, the gasoline from lower-level Karachukhursk petroleum contains 36.5% of paraffins and 33.5% of naphthenes. The paraffin-naphthene part of TsCh-1 contains 51.5% of paraffins and 48.5% of naphthenes. The naphthene part consists of 30.7% of cyclopentanes and 69.3% of cyclohexanes, i.e. the ratio of the amounts of cyclopentanes and cyclohexanes is 0.44. The proportions of the normal paraffins are (the total amount of normal paraffins being 100%) butane 1%, pentane 8.4%, hexane 22.7%, heptane 30.4%, and octane 37.5%, nonane is present, but has not been determined quantitatively. Of the $C_6$ branched paraffins present, 91.5% consists of methylpentanes, and only 8.5% of dimethylbutanes.

In the gasoline from lower-level Karachukhursk petroleum, as in the gasolines that we have investigated previously, there is very little cyclopentane. Of the cyclopentane hydrocarbons present, 3.8% is cyclopentane, 11.7% is methylcyclopentane, 40.7% consists of ethylcyclopentane and dimethylcyclopentanes, and 23.4% of $C_8$ cyclopentane hydrocarbons. The cyclohexane group consists mainly of $C_7$ and $C_8$ hydrocarbons. Of the cyclohexane hydrocarbons present, 10.8% is cyclohexane, 24.3% is methylcyclohexane, 27.6% consists of $C_8$ hydrocarbons, and 27.5% of $C_9$ hydrocarbons.

As in most of the gasolines investigated previously, among the aromatic hydrocarbons there is a predominance of $C_8$ compounds, i.e. ethylbenzene and xylenes. Of the aromatic hydrocarbons present, 6.3% is benzene, 34.3% is toluene, and 59.4% is represented by the xylene fraction. In this fraction there is more m-xylene than any other component, for of the $C_8$ hydrocarbons present, 26% is ethylbenzene, 40% is m-xylene, 20% is o-xylene, and 14% is p-xylene.

TABLE 2

Individual Hydrocarbons found in the Gasoline TsCh-1

| Hydrocarbon | Content (% by weight on TsCh-1) | Hydrocarbon | Content (% by weight on TsCh-1) |
|---|---|---|---|
| **Paraffin hydrocarbons** | | | |
| Butane | 0.14 | 2-Methylheptane | 2.10 |
| Pentane | 1.18 | 3-Methylheptane | 3.37 |
| 2-Methylbutane | 0.13 | 4-Methylheptane | 0.64 |
| Hexane | 3.17 | 2,2-Dimethylhexane | 0.36 |
| 2-Methylpentane | 1.00 | 2,3-Dimethylhexane | 0.40 |
| 3-Methylpentane | 0.83 | 2,5-Dimethylhexane | 0.74 |
| 2,2-Dimethylbutane | 0.11 | 2-Ethylhexane | 0.63 |
| 2,3-Dimethylbutane | 0.06 | Nonane | + |
| Heptane | 4.20 | 2-Methyloctane | 1.01 |
| 2-Methylhexane | 1.47 | 3-Methyloctane | 1.01 |
| 3-Methylhexane | 1.17 | 4-Methyloctane | 0.50 |
| 2,2-Dimethylpentane | 0.20 | 2,3-Dimethylheptane | 2.84 |
| 2,4-Dimethylpentane | 0.49 | 2,5-Dimethylheptane | 1.33 |
| 3,3-Dimethylpentane | 0.20 | 2,2,4-Trimethylhexane | 0.24 |
| 3-Ethylpentane | 0.24 | 2,3,5-Trimethylhexane | 0.24 |
| Octane | 5.24 | 2,4,4-Trimethylhexane | 0.23 |
| | | Total | 35.53 |
| **Cyclopentane hydrocarbons** | | | |
| Cyclopentane | 0.39 | Isopropylcyclopentane | 0.22 |
| Methylcyclopentane | 1.20 | $1^c, 2^t, 3^c$-Trimethylcyclopentane | 0.50 |
| Ethylcyclopentane | 1.35 | $1^t, 2^c, 3^c$-Trimethylcyclopentane | 0.49 |
| 1,1-Dimethylcyclopentane | 0.62 | $1^c, 2^t, 4^c$-Trimethylcyclopentane | 0.76 |
| cis-1,2-Dimethylcyclopentane | 0.20 | Other cyclopentane homologs | 1.48 |
| trans-1,2-Dimethylcyclopentane | 1.38 | Total | 10.25 |
| 1,3-Dimethylcyclopentane | 1.25 | | |
| Propylcyclopentane | 0.44 | | |
| **Cyclohexane hydrocarbons** | | | |
| Cyclohexane | 2.46 | 1-Ethyl-3-methylcyclohexane | 0.81 |
| Methylcyclohexane | 7.99 | 1-Ethyl-4-methylcyclohexane | 0.41 |
| Ethylcyclohexane | 4.24 | 1,1,3-Trimethylcyclohexane | 1.62 |
| 1,1-Dimethylcyclohexane | 0.40 | 1,2,3-Trimethylcyclohexane | 0.13 |
| 1,2-Dimethylcyclohexane | 1.55 | 1,2,4-Trimethylcyclohexane | 0.27 |
| 1,3-Dimethylcyclohexane | 1.69 | Total | 23.24 |
| 1,4-Dimethylcyclohexane | 0.85 | | |
| Propylcyclohexane | 0.41 | | |
| 1-Ethyl-2-methylcyclohexane | 0.41 | | |
| **Aromatic hydrocarbons** | | | |
| Benzene | 1.03 | o-Xylene | 1.96 |
| Toluene | 5.62 | m-Xylene | 3.93 |
| Ethylbenzene | 2.46 | p-Xylene | 1.37 |
| | | Total | 16.37 |

(Table continues on next page)

| | |
|---|---|
| Accounted for (% on TsCh-1) | 85.42 |
| Not accounted for quantitatively | 4.59 |
| Residues remaining after fractionations | 2.69 |
| Losses* | 7.30 |
| Total (% on TsCh-1) | 100.00 |

Group Composition of the Gasoline TsCh-1 (% on gasoline)

| | |
|---|---|
| Normal paraffins | 13.99 |
| Paraffins containing a tertiary carbon atom | 20.20 |
| Paraffins containing a quaternary carbon atom | 1.34 |
| Cyclopentanes | 10.28 |
| Cyclohexanes | 23.24 |
| Aromatics | 16.37 |

* Including small amounts of sulfur compounds contained in the original gasoline.

## EXPERIMENTAL *

The sample of gasoline ($n_D^{20}$ 1.4219; $d_4^{20}$ 0.7526; aniline point 43.7°; content of unsaturateds 1.3%; sulfur content 0.034% by weight) was regarded as a wide cut ShCh-1 and was fractionated through a 25-plate column. The results of the fractionation are given in Table 3 and Fig. 1. In this fractionation no gaseous part was obtained. The light and main fractions, taken together, formed the "whole gasoline" TsCh-1, amounting to 1637 g.

TABLE 3

| Fraction | Boiling limits (°C at 760 mm) | Weight (g) | Content of fraction (% by weight) | |
|---|---|---|---|---|
| | | | in ShCh-1 | in TsCh-1 |
| Taken for distillation | – | 1780 | 100.00 | – |
| LCh-1 (light fraction) | 23.8–55.5 | 36 | 2.02 | 2.20 |
| ACh-1 (main fraction) | 55.5–150.0 | 1601 | 89.94 | 97.80 |
| Residue | above 150 | 119 | 6.69 | – |
| Losses | – | 24 | 1.35 | – |

Investigation of the Light Fraction. After removal of sulfur compounds by chromatographic adsorption (the losses amounted to 0.05% on TsCh-1), the light fraction LCh-1 was distilled through a 40-plate column. Fractions were taken, and the fractionation curve (Fig. 2) was determined at the same time. The amounts of the fractions obtained, and their properties, are given in Table 4.

TABLE 4

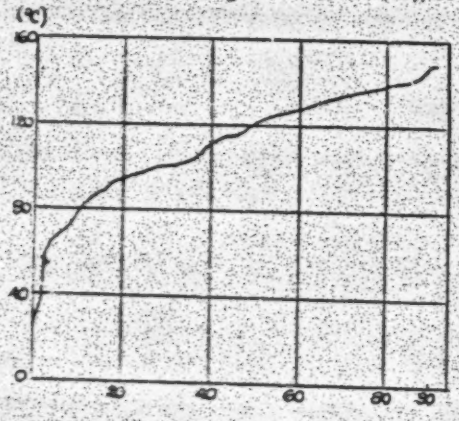
Results of the Fractionation of the Light Fraction LCh-1

| Fraction No. | Boiling limits (°C at 760 mm) | Weight (g) | $n_D^{20}$ | $d_4^{20}$ | Content of fraction (% by weight) | |
|---|---|---|---|---|---|---|
| | | | | | in LCh-1 | in TsCh-1 |
| Taken for fractionation | | 34.1 | | | 100.00 | 2.14 |
| | Butane (in coil) | 2.2 | – | – | 6.45 | 0.14 |
| I | 27.7–32.0 | 2.1 | 1.3528 | 0.6163 | 6.16 | 0.13 |
| II | 32.0–42.0 | 18.75 | 1.3572 | 0.6244 | 54.98 | 1.18 |
| | Residue | 7.9 | | | 23.17 | 0.50 |
| | Losses | 3.15 | | | 9.24 | 0.20 |

As can be seen from Table 4, the constants of Fraction I correspond to those of 2-methylbutane (b.p. 27.85°; $n_D^{20}$ 1.3537; $d_4^{20}$ 0.6197), and the constants of Fraction II are close to those of pentane (b.p. 36.07°; $n_D^{20}$ 1.3575; $d_4^{20}$ 0.6262). The residue from the fractionation of LCh-1, after removal of fluorescent substances by chromatographic adsorption (when it had $n_D^{20}$ 1.3887; $d_4^{20}$ 0.7157), was investigated by the Raman spectrum method. The results are given in Table 5. In the present communication we publish frequencies and visually estimated intensities of the spectrum lines of the narrow fractions. The qualitative compositions of the fractions were established from these data.

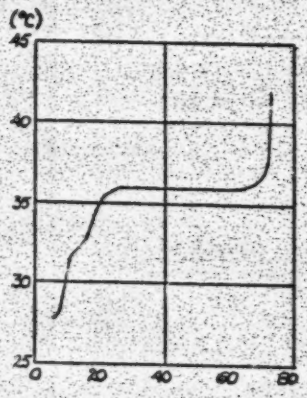
* Laboratory assistants T. V. Lapshina, K. G. Ryabova, and G. S. Taits took part in the experimental work.

Spectrum of residue $\Delta\nu$ (cm$^{-1}$)*: 325(3 b), 392(0), 445(3), 478(1); 505(0); 711(4); 731(1); 752(1 b); 785(1); [illegible]; 957(0); 997(0); 1024(0d); 936(1); 949(0); 960(0); 969(0); 983(0); 1017(2); 1028(6b); 1038(3); 1053(1); 1101(1); 1146(3b); 1173(2b); 1213(2b); 1220(0), 1249(2b), 1274(0b); 1282(1); 1299(3b); 1309(1); 1339(1b); 1364(0).




% by volume

Fig. 1. Fractionation curve for the gasoline ShCh-1.




% by volume

Fig. 2. Fractionation curve for the light fraction LCh-1.

In order to make quantitative determinations multiple photographs were taken of the spectra of the fractions and of the standard hydrocarbon and some of the lines were measured and their intensities determined from the laws of photographic photometry.

Separation of the Aromatic Hydrocarbons from the Mixture of Paraffins and Naphthenes in the Main Fraction ACh-1. Aromatics were separated from the A fraction ($n_D^{20}$ 1.4217; $d_4^{20}$ 0.7481; aniline point 42.5°; sulfur content 0.03%, content of unsaturateds 1.2%) with the aid of chromatographic adsorption on silica gel. Table 6 gives the amounts of the fractions both the amounts actually isolated, and the corrected amounts, i.e. corrected for the amounts used for qualitative tests for aromatics and for refractive index determinations. This table shows the results of the separation; also in Fig. 3 a curve is given for the variation in refractive index when 18 ml of Fraction A was passed through 80 g of silica gel.

The dearomatized fraction VCh-1 contained neither sulfur nor unsaturated hydrocarbons. The aromatic fraction, which contained sulfur, was again passed through the silica gel column. The fractions obtained had the following properties: BCh-1: $n_D^{20}$ 1.4276; $d_4^{20}$ 0.8606; aniline point 58.9°. VCh-1: $n_D^{20}$ 1.4092; $d_4^{20}$ 0.7348; aniline point 58.9°.

Investigation of the Aromatics BCh-1. The aromatic hydrocarbons (Fraction BCh-1) were fractionated through a 40 plate column into benzene, toluene, and xylene fractions, the fractionation curve (Fig. 4) being determined at the same time. In order to complete the distillation of the xylene fraction, pure decahydronaphthalene was added toward the end of the distillation.

We give below the Raman spectrum of the xylene fraction

$\Delta\nu$ (cm$^{-1}$): [illegible] 231(4), 256(2), 279(3), 311(2), 457(3s); 486(1), 504(2), 515(4); 537(7s), 582(5s), 623(1); [illegible] 727(4), [illegible] 784(3), 788(1), 813(2); 830(5); 858(0); 1001(9); 1031(3); 1053(6); 1096(2d); 1158(4b); [illegible] 1220(0), 1255(0), 1308(7), 1363(2), 1310(0b), 1378(7).

The results of the fractionation of the aromatics BCh-1 and the properties of the fractions are given in Table 7.

As will be seen from the data in Table 7, according to their physical properties, fraction I can be regarded as a benzene fraction, and fraction II as a toluene fraction; we may assume that the amounts of these fractions correspond to the contents of benzene and toluene in the gasoline. The results of the optical analysis of fraction II are given in Table 8.

Dehydrogenation of Cyclohexane Hydrocarbons. With the object of converting the cyclohexane hydrocarbons into aromatics, the paraffin-naphthene fraction VCh-1 was subjected to catalytic dehydrogenation, for which purpose it was passed over an iron-platinum catalyst at 300° at a space velocity of 0.9-1.0 liter per liter of catalyst per hour; at the same temperature and at a space velocity of 0.34, the catalyst dehydrogenated cyclohexane

* Symbols in parentheses, the numbers are intensities on a ten-grade scale, the letters have the following meanings: b - broad line, s - sharp line, d - doublet, g - background.

to the extent of 90%). The dehydrogenation of VCh-1 was complete in one passage. From 651.3 g of VCh-1, 611.8 g (93.94% on VCh-1) of catalyzate GCh-1 was obtained (611.3 g actually collected and 0.5 g used for tests). The amount of GCh-1 calculated on TsCh-1 was 75.01%.

TABLE 5

Results of the Optical Investigation of the Residue from the Light Fraction LCh-1

| Hydrocarbons found | Content (% by weight) | |
|---|---|---|
| | in residue | in whole gasoline TsCh-1 |
| Residue | 100 | 0.50 |
| Cyclopentane | 55 | 0.28 |
| 2-Methylpentane | 10 | 0.05 |
| 3-Methylpentane | 20 | 0.10 |
| 2,2-Dimethylbutane | 10 | 0.05 |
| 2,3-Dimethylbutane | 5 | 0.02 |

The losses (39.5 g i.e. 6.06% on VCh-1, or 4.84% on TsCh-1) included the hydrogen formed in the dehydrogenation of the cyclohexane hydrocarbons, the amount of which was not determined. After the experiment the catalyst still retained its activity, as indicated by its behavior in the dehydrogenation of cyclohexane.

The physical properties of the original fraction VCh-1 and of the dehydrogenation catalyzate GCh-1 were:

| | $n_D^{20}$ | $d_4^{20}$ | Aniline point (°C) |
|---|---|---|---|
| VCh-1 | 1.4092 | 0.7348 | 58.9 |
| GCh-1 | 1.4248 | 0.7543 | 39.5 |

The catalyzate GCh-1 contained a small amount of unsaturated hydrocarbons (1.4%).

Separation of the Catalyzate GCh-1 into Aromatic Hydrocarbons and a Mixture of Paraffins and Cyclopentanes. The catalyzate GCh-1 was separated chromatographically into an aromatic fraction DCh-1 and a paraffin-cyclopentane fraction ECh-1. The results of the separation of the catalyzate GCh-1 are given in Table 9.

The fractions separated, DCh-1 and ECh-1 (after removal of pentane by distillation), had the following properties:

| | $n_D^{20}$ | $d_4^{20}$ | Aniline point |
|---|---|---|---|
| Ch-1 | 1.4870 | 0.8666 | — |
| ECh-1 | 1.4029 | 0.7195 | 65.5 |

Investigation of the Aromatics DCh-1. Fraction DCh-1 was fractionated through a 40-plate column (similarly to the aromatic BCh-1). The results of the fractionation, the properties of separate fractions, and the results of the optical analysis, calculated back to the corresponding hydrocarbons, are given in Fig. 5 and Table 10. We give below the Raman spectra of Fractions III and IV.

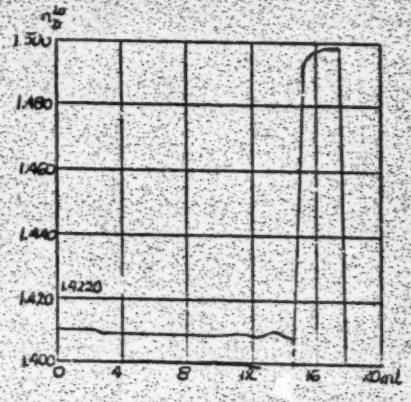



Fig. 3. Curve for the variation in refractive index during chromatographic separation of Fraction ACh-1.

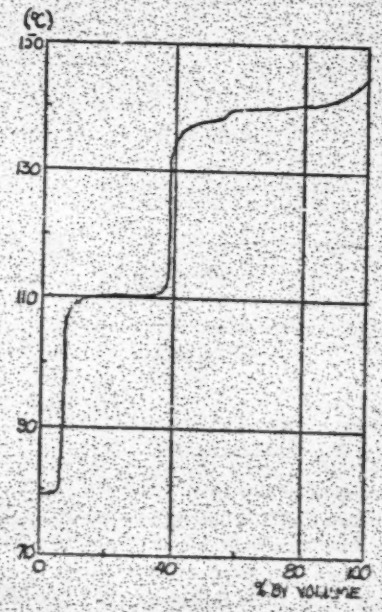



Fig. 4. Fractionation curve for the aromatic fraction BCh-1.

Frac. III: $\Delta\nu$ ($cm^{-1}$): 232(4b); 257(3b); 279(2b); 314(4b); 368(0d); 459(4s); 487(2d); 506(3s); 518(4s); 537(6s); 556(0s); 582(5s); 624(4); 646(2); 726(8s); 735(8s); 771(4); 788(3s); 813(2); 880(7); 917(2d); 980(1); 1003(10); 1032(6); 1053(7); 1097(1); 1157(3); 1181(1d); 1206(6); 1224(4); 1251(6s); 1267(1s); 1287(1d); 1328(1b); 1380(0);

Frac. IV, $\Delta\nu$ ($cm^{-1}$): 212(4b); 225(4b); 256(1); 282(1); 318(3); 420(0); 440(2); 473(2); 509(2d); 530(2); 554(3); 580(4); 620(1); 643(1); 658(2); 719(6s); 735(6s); 746(5s); 807(2d); 820(2d); 923(1); 972(1); 988(1); 1003(7); 1029(2);

1054.5(1); 1058.1(1); 1095(1); 1159(1); 1185(0); 1202(1); 1223(2); 1247(4); 1278(8); 1324(1b); 1382(6).

The data in Table 10 show also that Fraction I can be regarded as a benzene fraction, and Fraction II as a toluene fraction. From the amounts of these we can calculate the corresponding amounts of cyclohexane and methylcyclohexane, and also the amount of hydrogen that separated in the dehydrogenation (1.25% on TsCh-1).

TABLE 6

Chromatographic Separation of Fraction ACh-1

| Amount of fraction ACh-1 taken (g) | Results of Separation | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | Aromatics BCh-1 | | | | Paraffins and naphthenes VCh-1 | | | | Losses | | |
| | Actual (g) | Corrected (g) | (% in ACh-1) | (% in TsCh-1) | Actual (g) | Corrected (g) | (% in ACh-1) | (% in TsCh-1) | (g) | (% in ACh-1) | (% in TsCh-1) |
| 206.58 | 191.77 | 198.44 | 17.47 | 17.09 | 925.34 | 327.16 | 81.65 | 79.85 | 9.98 | 0.88 | 0.86 |

TABLE 7

Fractionation of the Aromatics BCh-1

| Fraction No. | Boiling limits (°C at 760 mm) | Weight (g) | $n_D^{20}$ | $d_4^{20}$ | Content of fraction (% by weight) | |
|---|---|---|---|---|---|---|
| | | | | | in BCh-1 | in TsCh-1 |
| Taken for fractionation | | 187.4 | 1.4978 | .8666 | 100.00 | 17.09 |
| I | 74.1–92.9 | 11.3 | 1.4970 | 0.8895 | 6.03 | 1.03 |
| II | 92.9–128.0 | 60.5 | 1.4937 | 0.8664 | 32.28 | 5.52 |
| III | 128.0–143.4 | 107.7 | 1.4991 | 0.8680 | 57.47 | 9.82 |
| | Residue | 2.0 | | | 1.07 | 0.18 |
| | Losses | 5.9 | | | 3.15 | 0.54 |

TABLE 8

Results of the Optical Analysis of Fraction III

| | Content of hydrocarbon (% by weight) | |
|---|---|---|
| | in Fraction III | in TsCh-1 |
| Benzene | 100 | 9.82 |
| Toluene | 1 | 0.10 |
| o-Xylene | 20 | 1.96 |
| m-Xylene | 40 | 3.93 |
| p-Xylene | 14 | 1.37 |
| Ethylbenzene | 25 | 2.46 |

Investigation of Paraffin-Cyclopentane Fraction ECh-1. A portion (100 ml) of the paraffin-cyclopentane fraction was fractionated through a 50-plate column in order to determine the fractionation curve. The distillation was carried out at a reflux ratio of 45-50 with continuous separation of distillate. The fractionation curve is given in Fig. 6. The vertical lines indicate the limits between which narrow fractions were taken in the subsequent fractionation; the selection of these limits was determined by the form of the fractionation curve and by the boiling points of individual hydrocarbons.

When the fractionation curve had been determined, 300 ml of Fraction ECh-1 was fractionated through the same column with continuous separation of distillate and at a reflux ratio of 40-45. Altogether, 15 narrow fractions were taken. The results of the fractionation of the paraffin-cyclopentane fraction into narrow fractions and the properties of these fractions are given in Table 11. The Raman spectra of these fractions are given below.

TABLE 9

Chromatographic Separation of the Catalyzate GCh-1

| Catalyzate GCh-1 taken (g) | Results of separation | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | Aromatics DCh-1 | | | | Paraffin-cyclopentane fraction ECh-1 | | | | Losses | | |
| | Actual (g) | Corrected (g) | (% in GCh-1) | (% in TsCh-1) | Actual (g) | Corrected (g) | (% in GCh-1) | (% in TsCh-1) | (g) | (% in GCh-1) | (% in TsCh-1) |
| 500.00 | 152.59 | 156.16 | 30.67 | 22.16 | 421.10 | 421.78 | 71.20 | 53.78 | 8.43 | 1.43 | 1.07 |

The results of the quantitative optical analysis, which was in close accord with the physical properties of the narrow fractions, are given in Table 12.

TABLE 10

Fractionation of the Aromatics DCh-1

| Fraction No. | Boiling limits (°C at 760 mm) | Weight (g) | $n_D^{20}$ | $d_4^{20}$ | Content of fraction (% by weight on DCh-1) | Content of fraction of corresponding cyclohexanes (% by weight on TsCh-1) |
|---|---|---|---|---|---|---|
| Taken for fractionation | | 43.0 | 1.4970 | 0.8666 | 100.00 | |
| I | 78.0–100.3 | 4.7 | 1.4958 | 0.8695 | 10.93 | 2.37 |
| II | 100.3–128.4 | 15.1 | 1.4956 | 0.8640 | 35.12 | 7.54 |
| III | 128.4–147.4 | 17.1 | 1.4978 | 0.8672 | 39.77 | 8.48 |
| IV | 147.4–167.3 | 5.5 | 1.4996 | 0.8701 | 12.79 | 2.71 |
| | Residue | 0.0 | | | 0.00 | 0.00 |
| | Losses | 0.6 | | | 1.39 | 0.30 |

Results of the Optical Analysis of Fraction III of DCh-1

| Content of aromatic hydrocarbons (% by weight on Fraction III) | | Content of corresponding cyclohexane hydrocarbons (% by weight on TsCh-1) | |
|---|---|---|---|
| Toluene | 5 | Methylcyclohexane | 0.42 |
| o-Xylene | 15 | 1,2-Dimethylcyclohexane | 1.28 |
| m-Xylene | 20 | 1,3-Dimethylcyclohexane | 1.69 |
| p-Xylene | 10 | 1,4-Dimethylcyclohexane | 0.85 |
| Ethylbenzene | 50 | Ethylcyclohexane | 4.24 |

Results of the Optical Analysis of Fraction IV of DCh-1

| Content of aromatic hydrocarbons (% by weight on Fraction IV) | | Content of corresponding cyclohexane hydrocarbons (% by weight on TsCh-1) | |
|---|---|---|---|
| Propylbenzene | 15 | Propylcyclohexane | 0.41 |
| 1-Ethyl-2-methylbenzene | 15 | 1-Ethyl-2-methylcyclohexane | 0.41 |
| 1-Ethyl-3-methylbenzene | 30 | 1-Ethyl-3-methylcyclohexane | 0.81 |
| 1-Ethyl-4-methylbenzene | 15 | 1-Ethyl-4-methylcyclohexane | 0.41 |
| o-Xylene | 10 | 1,2-Dimethylcyclohexane | 0.27 |
| 1,2,4-Trimethylbenzene | 10 | 1,2,4-Trimethylcyclohexane | 0.27 |
| 1,2,3-Trimethylbenzene | 5 | 1,2,3-Trimethylcyclohexane | 0.13 |

All of the data obtained in the course of the investigation for the contents of the individual hydrocarbons, expressed as percent by weight on the whole gasoline TsCh-1, are given in Table 2. The same table shows the overall balance sheet for the investigation.

Δν (cm$^{-1}$) Frac. I: 262(5); 326(3b); 370(1); 391(1); 440(6s); 479(1); 546(0); 580(0); 711(1); 731(4); 748(3b); 763(1); 781(0); 794(1); 812(8); 863(0b); 887(6b); 922(0); 937(1b); 956(4); 981(2b); 1015(2b); 1036(7); 1071(1b); 1145(5b); 1167(5b); 1196(0); 1245(0); 1277(1b); 1299(5b); 1343(3b); 1355(2b).

Frac. II: 306(1b); 314(3b); 326(1b); 340(1); 372(2); 493(1); 533(3); 810(3b); 825(4b); 838(3b); 846(1); 870(2); 891(6b); 979(2); 1010(2); 1039(3); 1065(0); 1083(4b); 1135(2b); 1162(0); 1191(1b); 1278(2b); 1382(6b); 1353(1b).

Frac. III: 253(0); 306(2); 324(1); 349(1); 372(0); 410(0); 433(2b); 468(0); 495(1); 530(1b); 559(1); 692(2); 767(0); 784(1); 801(6s); 807(5); 823(2); 846(1); 899(5); 915(0); 922(2); 938(2); 956(3); 984(0); 1006(0); 1027(4); 1042(1); 1057(1); 1089(3); 1698(3); 1146(5b); 1161(4b); 1172(4b); 1191(3b); 1207(2); 1247(1); 1264(1); 1301(4b); 1317(2); 1329(3); 1340(3).

Frac. IV: 263(0); 283(0); 312(2); 322(1); 347(1); 377(1b); 397(0); 416(0); 432(3b); 446(2); 496(4); 513(1b); 526(0); 557(0); 716(1); 739(1); 768(4); 784(2); 800(3); 824(5); 864(1); 877(1); 897(6); 930(0); 945(0); 957(3); 983(4); 993(5); 1018(1); 1030(3); 1044(4b); 1064(0); 1074(2); 1080(6b); 1086(2); 1101(3); 1146(5b); 1173(4b); 1187(0); 1226(0); 1250(0); 1285(1); 1301(7b); 1340(6b); 1348(2); 1355(4b).

Frac. V: 295(0), 312(4), 357(0), 328(2b), 139(1), 469(1), 499(3), 527(0), 735(2b), 767(4b), 801(2), 833(4b), 867(3b), 897(1), 898(6b), 932(2), 956(2), 983(1), 1023(4b), 1039(3b), 1082(7b), 1104(1), 1139(7b), 1167(1), 1202(1), 1225(1), 1302(8), 1338(2), 1366(0).

Frac. VI: 283(0), 312(5), 351(0), 358(0), 394(2), 402(2), 455(0), 501(2), 585(0), 603(0), 679(0), 694(0), 727(0), 738(0), 761(0), 774(3), 824(2), 835(5b), 853(4b), 888(4), 902(6), 933(2), 949(2g), 960(2g), 981(1), 1024(2), 1043(3), 1064(2), 1079(3), 1105(1), 1136(5), 1162(2), 1195(2), 1236(1), 1267(2), 1281(1), 1303(8b), 1346(0), 1386(2b).

Frac. VII: 263(0), 272(0), 287(0), 309(2), 339(1), 366(0), 396(3b), 408(2), 415(3b), 425(1), 444(1b), 482(1), 494(4), 521(2), 718(0), 746(2), 768(5), 795(1), 802(2g), 814(1), 838(3), 852(1), 874(2), 892(4), 902(1g), 927(2), 937(2), 946(2), 958(2), 968(1), 992(1), 1014(2), 1024(3), 1043(3), 1056(2b), 1069(2), 1083(2), 1088(2), 1103(1), 1135(2), 1146(1), 1162(2), 1180(2), 1203(0), 1234(0), 1250(0), 1267(1), 1295(4), 1305(4), 1318(3), 1336(2), 1354(2).

Frac. VIII: 239(1b), 266(0), 287(1), 317(2), 330(0), 405(1), 418(0), 428(0), 443(1), 460(0), 493(4), 521(3), 552(0), 598(0), 607(1), 616(0), 671(0), 685(0), 717(0), 723(0), 733(0), 756(1), 768(5), 780(1), 816(4), 834(2), 858(0), 877(2), 902(2), 979(1g), 946(2g), 956(4b), 991(0), 1008(0), 1025(1), 1042(3), 1058(0), 1080(1b), 1100(2b), 1143(4b), 1157(4b), 1172(2), 1191(2b), 1202(1), 1246(0), 1274(0), 1305(4), 1324(1), 1337(3), 1352(2).

Frac. IX: 247(5), 259(1), 269(1), 278(1), 288(3), 298(2), 314(2), 322(2), 328(0), 350(1b), 370(1g), 384(1g), 407(2g), 417(1), 429(2g), 432(1), 440(1), 446(1), 489(1), 513(1), 548(0), 560(0), 573(0), 676(0), 703(5s), 729(2), 746(2), 762(4b), 795(0), 814(3b), 822(2), 830(1), 839(1), 858(0), 869(2), 877(1), 892(3), 904(2), 934(1), 944(0), 956(3b), 970(2b), 980(1), 1008(2), 1029(1), 1043(3), 1060(0), 1077(4), 1099(1), 1110(1), 1126(0), 1143(5), 1154(3b), 1164(1), 1175(1), 1190(2b), 1244(2b), 1267(1b), 1301(5b), 1338(3), 1360(2b).

Frac. X: 246(0), 260(0), 282(3), 296(1), 316(1), 323(0), 372(0), 401(0), 416(1), 426(1), 448(1), 460(1b), 492(1), 513(0), 525(1), 556(1), 580(0), 597(0), 645(0), 704(5), 730(0), 747(0), 759(2), 768(1), 795(0), 806(2), 819(2), 828(1), 841(0), 851(0), 860(0), 875(2), 884(4), 907(1), 917(0), 938(1b), 964(3), 972(2), 985(1), 1028(3b), 1039(3b), 1048(1), 1056(1), 1066(1), 1078(3), 1088(2), 1124(2), 1145(0), 1161(1), 1171(0), 1193(2), 1223(0), 1242(1), 1257(0), 1264(1), 1282(1), 1302(5b), 1343(1), 1351(1).

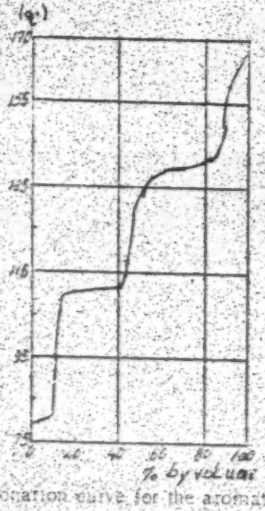



Fig. 5 Fractionation curve for the aromatics DCH-1

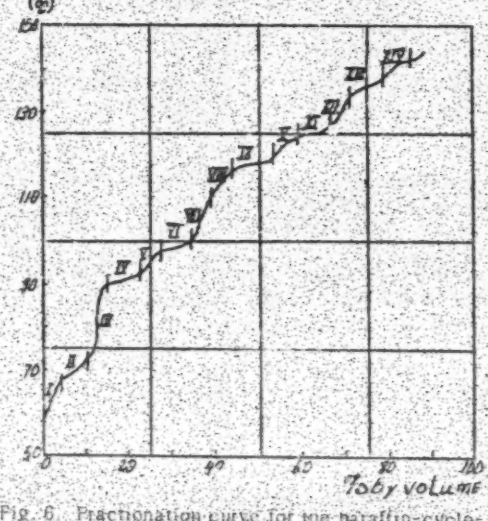



Fig. 6 Fractionation curve for the paraffin-cyclopentane fraction, ECH-1

Frac. XI: 245(2), 264(0), 292(6), 295(1b), 306(0), 318(0), 334(0), 352(0), 372(1b), 393(0), 403(0), 414(1), 427(2), 436(0), 449(1), 511(0), 521(0), 529(0), 544(0), 562(0), 579(0), 590(0), 625(0), 668(0), 696(0), 705(1), 719(0), 730(1), 750(2), 764(2), 804(2), 817(2), 841(3), 850(4), 875(4), 895(5), 923(5), 932(0), 956(2), 967(2), 982(0), 1003(0), 1020(3), 1043(3), 1057(5), 1092(7), 1107(6), 1125(5s), 1153(1), 1164(2), 1198(2), 1222(0), 1240(0), 1254(0), 1273(1), 1303(8), 1341(1).

TABLE 11

Results of the Fractionation of the Paraffin-Cyclopentane Fraction ECh-1

| Fraction No. | Boiling limits (°C at 760 mm) | Weight (g) | Content of fraction (% by weight) | | $n_D^{20}$ | $d_4^{20}$ | Aniline point (°C) |
|---|---|---|---|---|---|---|---|
| | | | in ECh-1 | in TsCh-1 | | | |
| Taken for fractionation . . . . . | | 218.5 | 100.00 | 53.76 | 1.4029 | 0.7195 | – |
| I | 42.3–67.0 | 8.5 | 3.89 | 2.09 | 1.3753 | 0.6622 | 68.2 |
| II | 67.0–72.0 | 16.5 | 7.55 | 4.06 | 1.3896 | 0.6972 | 53.4 |
| III | 72.0–90.0 | 8.0 | 3.66 | 1.97 | 1.3980 | 0.7142 | 57.6 |
| IV | 90.0–92.5 | 19.0 | 8.70 | 4.68 | 1.3977 | 0.7129 | 60.5 |
| V | 92.5–98.0 | 6.4 | 2.93 | 1.58 | 1.3936 | 0.7011 | 63.8 |
| VI | 98.0–99.5 | 16.2 | 7.41 | 3.99 | 1.3902 | 0.6907 | 67.1 |
| VII | 99.5–110.0 | 9.8 | 4.44 | 2.39 | 1.4068 | 0.7335 | 52.6 |
| VIII | 110.0–117.0 | 10.8 | 4.94 | 2.66 | 1.4047 | 0.7250 | 66.3 |
| IX | 117.0–120.0 | 19.7 | 9.02 | 4.85 | 1.4033 | 0.7191 | 67.6 |
| X | 120.0–124.5 | 12.9 | 5.90 | 3.17 | 1.4053 | 0.7245 | 65.5 |
| XI | 124.5–126.5 | 20.0 | 9.15 | 4.92 | 1.4002 | 0.7113 | 69.6 |
| XII | 126.5–133.5 | 7.2 | 3.30 | 1.77 | 1.4100 | 0.7350 | 66.2 |
| XIII | 133.5–138.0 | 18.0 | 8.24 | 4.43 | 1.4182 | 0.7537 | 64.3 |
| XIV | 138.0–143.0 | 20.5 | 9.38 | 5.04 | 1.4123 | 0.7377 | 69.6 |
| XV | 143.0–148.5 | 12.1 | 5.54 | 2.98 | 1.4150 | 0.7428 | 67.5 |
| | Residue | 10.2 | 4.67 | 2.51 | | | |
| | Losses | 2.8 | 1.28 | 0.69 | | | |

Frac. XII: 249(0); 264(0); 282(3), 300(0); 321(1b); 332(1); 342(1); 362(1); 401(0); 420(1); 437(0); 455(1); 469(1); 480(1); 498(1); 534(0); 555(1s); 645(0); 682(0); 708(1), 726(3s); 743(2); 762(3b); 790(2), 815(4bg), 820(2); 828(1); 840(3g); 862(2g), 878(2g); 896(6s); 927(1bg); 956(3b); 973(2b); 1001(0), 1016(1), 1031(3g); 1043(2), 1058(3g); 1085(4b), 1093(2b); 1107(2); 1130(1); 1141(b); 1166(5b); 1192(4); 1216(1); 1252(2); 1277(0b); 1303(8); 1323(1), 1341(2b), 1356(1); 1394(1b)

Frac. XIII: 250(1h); 263(0); 301(0); 324(3); 345(0g); 368(0b); 398(0), 422(2g); 436(2g); 465(3); 499(1); 519(1); 556(6); 629(0); 689(1); 726(7s); 749(0b); 766(5); 786(1b); 796(3); 806(3); 814(3), 837(3b); 850(1); 869(1b) 896(3); 905(2), 935(4); 954(4), 974(4b); 982(4b); 1009(0), 1017(1); 1032(1b); 1097(3b); 1145(4b), 1168(4b); 1190(5); 1220(2); 1247(3); 1281(3b), 1295(5b); 1306(4b); 1320(2), 1341(5b), 1355(3b), 1381(2b).

Frac. XIV: 257(1b); 286(1b); 297(0); 310(0); 324(0); 344(0), 379(0); 398(0), 429(1b), 461(1b); 511(1); 555(1); 576(1), 591(0); 619(1), 707(1); 726(3g); 759(3g), 769(3g); 797(1dg); 813(2); 822(2); 842(1dg); 857(1); 874(3bg); 892(4bg), 918(2); 927(2b); 938(2b); 954(3dg); 977(1dg); 1001(1dg); 1022(2), 1040(4 b. polarized), 1057(5 b. polarized), 1079(5 polarized); 1104(1b), 1140(5b); 1160(6b); 1191(3d); 1248(1d); 1276(1d), 1301(7b); 1344(4b); 1355(2b); 1386(2b).

Frac. XV: 250(2); 266(2); 283(2); 318(0); 342(0); 354(0); 382(0); 407(0); 416(0); 434(1); 454(0), 512(2b); 527(1g), 540(1g); 560(1g), 583(1g); 599(1b); 625(0); 648(0); 679(4); 712(0), 728(3); 745(2g); 766(1g); 790(1g); 815(4bg); 822(2); 834(4bg); 846(2b); 871(4); 892(5b); 909(1b); 920(0); 934(1); 953(2g); 970(2g); 980(1g), 1003(0b), 1014(1b); 1043(3b), 1060(2g); 1082(6b); 1137(6b); 1147(3); 1160(3b), 1189(0), 1201(1), 1242(1); 1273(1b), 1303(7b); 1346(3b); 1382(2b).

The results of the quantitative optical analysis, which was in close accord with the physical properties of the narrow fractions, are given in Table 12. All of the data obtained in the course of the investigation for the contents of the individual hydrocarbons, expressed as per cent by weight on the whole gasoline TsCh-1, are given in Table 2. The same table shows the overall balance sheet for the investigation.

## SUMMARY

1. By means of the combination method of investigating the individual hydrocarbon compositions of straight-run gasolines, an analysis has been made of a gasoline having an upper boiling limit of 150° derived from lower-level Karachukhursk petroleum.

2. The individual hydrocarbon composition of the Karachukhursk gasoline has been accounted for quantitatively to the extent of 85.4% (by weight on the whole gasoline). The total losses in analysis were 7.30%, the residues in the distillation flasks amounted to 2.69% and the composition of 4.59% of the gasoline remained undetermined. Altogether, 63 hydrocarbons have been determined quantitatively.

TABLE 12

Results of the Optical Investigation of Narrow Fractions of the Paraffin-Cyclopentane Fraction ECh-1

| Hydrocarbons found optically | Content of hydrocarbon (% by weight) | |
|---|---|---|
| | in fraction | in TsCh-1 |
| **Fraction I** | | |
| Cyclopentane | 5 | 0.10 |
| 2,2-Dimethylbutane | 3 | 0.06 |
| 2,3-Dimethylbutane | 2 | 0.04 |
| 2-Methylpentane | 45 | 0.95 |
| 3-Methylpentane | 35 | 0.73 |
| Hexane | 10 | 0.21 |
| **Fraction II** | | |
| Hexane | 73 | 2.96 |
| Methylcyclopentane | 27 | 1.10 |
| **Fraction III** | | |
| Methylcyclopentane | 5 | 0.10 |
| 2,2-Dimethylpentane | 10 | 0.20 |
| 2,4-Dimethylpentane | 25 | 0.49 |
| Cyclohexane | 5 | 0.09 |
| 3,3-Dimethylpentane | 10 | 0.20 |
| 1,1-Dimethylcyclopentane | 20 | 0.39 |
| 2-Methylhexane | 15 | 0.30 |
| trans-1,2-Dimethylcyclopentane | 10 | 0.20 |
| **Fraction IV** | | |
| 1,1-Dimethylcyclopentane | 5 | 0.23 |
| 2-Methylhexane | 25 | 1.17 |
| 2,3-Dimethylcyclopentane | 25 | 1.17 |
| 3-Methylhexane | 25 | 1.17 |
| trans-1,2-Dimethylcyclopentane | 20 | 0.94 |
| **Fraction V*** | | |
| 1,1-Dimethylcyclopentane | 5 | 0.08 |
| trans-1,2-Dimethylcyclopentane | 15 | 0.24 |
| 3-Ethylpentane | 15 | 0.24 |
| Heptane | 60 | 0.95 |
| **Fraction VI*** | | |
| Heptane | 80 | 3.19 |
| cis-1,2-Dimethylcyclopentane | 5 | 0.20 |
| Ethylcyclopentane | 10 | 0.40 |
| **Fraction VII** | | |
| Heptane | 5 | 0.12 |
| Methylcyclohexane | 1–2 | 0.03 |
| Ethylcyclopentane | 40 | 0.95 |
| 2,2-Dimethylhexane | 15 | 0.38 |
| $1^c,2^t,4^c$-Trimethylcyclopentane | 10 | 0.23 |
| 2,5-Dimethylhexane | 20 | 0.47 |
| $1^c,2^t,4^c$-Trimethylcyclopentane | 10 | 0.23 |
| **Fraction VIII** | | |
| $1^c,2^t,4^c$-Trimethylcyclopentane | 20 | 0.53 |
| 2,5-Dimethylhexane | 10 | 0.27 |
| $1^c,2^t,3^c$-Trimethylcyclopentane | 10 | 0.27 |
| 2,3-Dimethylhexane | 15 | 0.40 |
| 2-Methylhexane | 25 | 0.65 |
| 4-Methylhexane | 10 | 0.27 |
| 3-Ethylhexane | 10 | 0.27 |
| **Fraction IX** | | |
| 2-Methylheptane | 30 | 1.45 |
| 4-Methylheptane | 15 | 0.73 |
| 3-Ethylhexane | | |
| $1^t,2^c,3^c$-Trimethylcyclopentane | 10 | 0.49 |
| 3-Methylheptane | 40 | 1.94 |
| 1,1-Dimethylcyclohexane | 5 | 0.24 |
| **Fraction X*** | | |
| 3-Methylheptane | 45 | 1.43 |
| 1,1-Dimethylcyclohexane | 5 | 0.16 |
| Octane | 40 | 1.27 |
| **Fraction XI** | | |
| Octane | 70 | 3.44 |
| Cyclopentane homologs** | 30 | 1.48 |

* Some lines have not been interpreted.

** It was not found possible to establish the composition of the cyclopentane homologs more exactly.

TABLE 12 (continued)

| Hydrocarbons found optically | Content of hydrocarbon (% by weight) | | Hydrocarbons found optically | Content of hydrocarbon (% by weight) | |
|---|---|---|---|---|---|
| | in the fraction | in TsCh-1 | | in the fraction | in TsCh-1 |
| Fraction XII* | | | Fraction XIV* | | |
| Octane | 30 | 0.53 | 1,1,3-Trimethylcyclohexane | 10 | 0.51 |
| Isopropylcyclopentane, Propylcyclopentane | 25 | 0.44 | 2,3-Dimethylheptane | 30 | 1.51 |
| | | | 4-Methyloctane | 10 | 0.50 |
| 2,2,4-Trimethylhexane, 2,3,5-Trimethylhexane, 2,4,4-Trimethylhexane | 40 | 0.71 | 2-Methyloctane | 20 | 1.01 |
| | | | 3-Methyloctane | 20 | 1.01 |
| Fraction XIII* | | | Fraction XV*** | | |
| Propylcylopentane | 5 | 0.22 | 4-Methyloctane, 2-Methyloctane, 3-Methyloctane | | |
| 2,5-Dimethylheptane, 2,3-Dimethylheptane | 60 | 2.66 | | | |
| 1,1,3-Trimethylcyclohexane | 25 | 1.11 | Nonane | | |

* Some lines have not been interpreted

*** Many of the lines have not been interpreted. The components could not be accounted for quantitatively owing to the diffuse character of the lines.

SUMMARY (continued)

3. There is a considerable amount of aromatic hydrocarbons in the gasoline derived from lower-level Karachukhursk petroleum (more than in any of the gasolines investigated previously by this method [2-4]), namely 16.37%. There are approximately equal amounts of paraffin and naphthene hydrocarbons in the gasoline. Of the total amount of paraffin hydrocarbons, 40% consists of normal paraffins. The ratio of the amounts of cyclopentane and cyclohexane hydrocarbons is 0.44.

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* See Consultants Bureau English translation page 215.
** See Consultants Bureau English translation page 225.
*** See Consultants Bureau English translation, page 387.
**** See Consultants Bureau English translation page 747.

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# HIGH-TEMPERATURE REACTIONS OF HEPTANE IN A CONTINUOUS-FLOW SYSTEM IN PRESENCE OF METALS OF THE PALLADIUM GROUP AND OF HYDROGEN AT HIGH PRESSURE

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The reactions of heptane in presence of hydrogen at high pressure have been studied in presence of platinum and nickel catalysts. Haensel and Donaldson [1], for example, investigated the reactions of heptane at 459° in presence of a platinum catalyst and hydrogen at a pressure of 35 atm. They found that, under these conditions, heptane yielded a complex mixture of paraffins, mainly of branched structure. Also, toluene in an amount corresponding to about 2% of the original heptane was found in the reaction products, and about 12.5% of the heptane was recovered unchanged.

The reactions of heptane at 460° in presence of platinized alumina and hydrogen at 20 atm in a flow system were investigated by Shuikin, Berdnikova, and Novikov [2]. These authors found that, apart from 12.2% of unchanged heptane, the catalyzate contained $C_5$-$C_7$ branched paraffins. In addition to the isomerization and cleavage reactions of the original hydrocarbon, the formation of a considerable amount (18%) of aromatic hydrocarbons was observed, and these included not only toluene, but also benzene, xylenes, and higher benzene homologs, which were not investigated in detail.

Ciapetta and Hunter [3] have recently investigated the reactions of heptane at 285-420° in presence of nickel on an aluminosilicate carrier and of hydrogen at 24.8 atm. At 353° the amount of $C_7$ branched hydrocarbons attained 67.2% and this included 3-methylhexane, 2-methylhexane, and 2,4-dimethylpentane. Hydrocarbons of lower molecular weight were also formed.

The data in these papers show that platinum and nickel, depending on the nature of the carrier and the experimental conditions, are able to promote a variety of reactions of heptane. The present investigation forms a continuation of our study [4] of the specific features of the behavior of carrier-supported metal catalysts of low active-metal content in the hydrogenation and dehydrogenation reactions of hydrocarbons. We have now studied the behavior of heptane in presence of Ru, Rh, Pd, and Pt deposited on silica gel. It should be noted that the reactions of paraffins in presence of Ru and Rh catalysts have not been investigated previously.

Our experiments have shown that, at a high temperature and a high pressure of hydrogen in a continuous-flow system in presence of the catalysts investigated, heptane undergoes far-reaching transformations. The greatest extent of conversion of the heptane into isomeric paraffins and aromatic hydrocarbons is observed in presence of Pt and Pd. Under the given conditions, rhodium and ruthenium catalysts, while promoting the formation of small amounts of isomeric paraffins, cause considerable degradation, mainly to methane.

## EXPERIMENTAL

Preparation of Catalysts. All catalysts were prepared by the same method under identical conditions. The silica gel, after being treated with dilute hydrochloric acid and washed with water, was heated at 500-550° for two hours. The catalysts were reduced at atmospheric pressure in a current of electrolytic hydrogen at 320-340° for eight hours.

Apparatus and Experimental Conditions

The experiments with n-heptane [b.p. (corrected) 98.5°; $n_D^{20}$ 1.3874; $d_4^{20}$ 0.6840] were carried out in a specially

* The spectroscopic part of this work was carried out in the Molecular Spectroscopy Laboratory of the Chemistry Department of the Moscow State University under the supervision of V. M. Tatevsky. The authors are very grateful to V. M. Tatevsky for discussions of the results of the spectroscopic determinations and for his help in the investigation.

constructed apparatus, which is shown diagrammatically in Fig. 1. The reactor 1 is a seamless steel tube of internal diameter 22 mm contained in an aluminum-bronze block heated by an electric resistance furnace. The temperature was measured with a thermocouple placed in a pocket in the reactor and was maintained at the required value within ± 3° by the aid of an electronic regulator. The hydrocarbon was passed to the reactor from the buret 3 with the aid of the dosing device 2. The latter consists of three cylinders containing pistons connected together by one common coupling rod. The piston in the middle cylinder is moved by oil delivered by the pump 4. When the piston moves from left to right, the hydrocarbon is drawn from the buret 3 into the void of the left cylinder of the dosing device, and at the same time hydrocarbon is forced from the right cylinder into the reactor. The ratio of the area of the piston of the middle cylinder to that of the left or right piston is 5:1, ensuring a low dosage rate (20 ml per hour). A low rate of dosage cannot be obtained by the direct use of the pump 3 owing to its comparatively high productivity (the lowest rate of dosage of pump 3 was 100 ml per hour) and to the lack of a satisfactory packing gland for working with low-boiling hydrocarbons. The required amount of hydrogen was passed into the reactor through the special flowmeter 7, which was graduated for the measurement of the flow of hydrogen at the experimental pressure. The catalysis products passed into the coil condenser 8 and then to the separator-receiver 9, in which the liquid hydrocarbons were separated from the gaseous products, which were passed through the gas meter 10, and then to the atmosphere or to a gas holder for analysis.

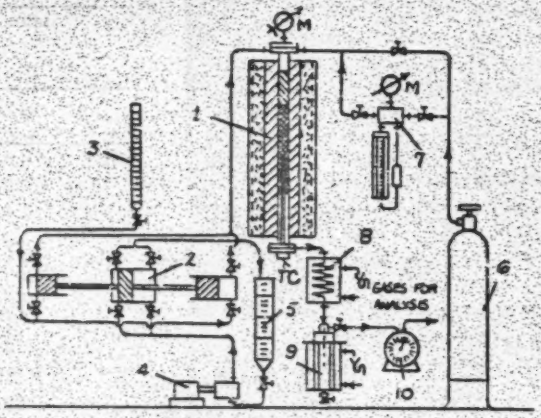



Fig. 1. Diagram of small-scale apparatus for the high-pressure reactions of hydrocarbons. 1 - reactor; 2 - dosing device; 3 - buret; 4 - pump; 5 - buret; 6 - cylinder of hydrogen; 7 - flowmeter; 8 - condenser; 9 - separator-receiver; 10 - gas meter; M - manometer; TC - thermocouple.

All experiments were carried out at 460°, the hydrogen pressure was 20 atm, and the space velocity for the passage of heptane was 1.1 liters per liter of catalyst per hour. The molar ratio of hydrogen to heptane was 5:1. The amount of each catalyst taken was 50 ml.

## Investigation of Catalyzates

The liquid catalyzates were characterized by determinations of specific gravity, refractive index, and content of aromatics (by the sulfuric acid method). Hydrocarbons boiling up to 40° were first removed from the catalyzate by distillation through a 45-plate column. The aromatic hydrocarbons were then separated by chromatographic adsorption on silica gel [5], and they were fractionated through a 33-plate column. Benzene homologs were subjected to Ullmann oxidation and were identified from the melting points of the acids obtained. Paraffins were separated into fractions with the aid of a 45-plate column, and these were investigated by the Raman spectrum method (the procedure and apparatus are described in the paper [6]). The gas was analyzed in an Orsat-Lunge apparatus.

Table 1 gives the properties of catalyzates obtained by the passage of heptane in presence of Pt, Pd, Rh, and Ru catalysts. It will be seen that the catalysts studied can be placed in the following order with respect to the amount of aromatic hydrocarbons formed from heptane in contact with them: Pt > Pd > Rh > Ru, whereas with respect to gas formation they must be placed in the reverse order: Ru > Rh > Pt > Pd.

Table 2 gives the properties of hydrocarbons boiling up to 40° which have been separated from the catalyzates. Comparison of the properties of the catalyzate obtained in the platinized silica gel experiment with data reported in the literature shows that the first fraction consisted mainly of isopentane, and the second mainly of n-pentane. The 33-41° fraction separated from the catalyzate obtained in the experiment with Pd-$SiO_2$ boiled mainly in the range 34-35°, it consisted almost entirely of n-pentane. In the heptane catalyzates obtained in the experiments with Rh and Ru catalysts, no hydrocarbons boiling below 40° were present.

Table 3 gives the fractional composition of the paraffin part of the heptane catalyzates, and Fig. 2 shows the fractionation curve for the paraffin part of the catalyzate obtained over Pt-$SiO_2$. Many of the fractions were investigated with the aid of their Raman spectra [6]. Thus, in the catalyzate obtained in the presence of platinized silica gel, the following hydrocarbons were identified. In Fractions I and II: 2-methylpentane 95-97% and 2,2-dimethylbutane 5-3%. In Fraction III: 2-methylpentane 45-50% and 3-methylpentane 55-50%. In Fraction IV: essentially hexane. In Fraction V: 2,4-dimethylpentane 16%, 2-methylhexane 30%, 3,3-dimethylpentane 12%, and 2,3-dimethylpentane 42%. In Fraction VI: 2-methylhexane 60-60% and 3-methylhexane 59-40%. Fractions VII and VIII were not investigated, since

they corresponded, according to their properties, to almost pure heptane.

TABLE 1

Properties of Heptane Catalyzates obtained with Pt, Pd, Rh, and Ru Catalysts

| No. | Catalyst | Amount of substance passed (g) | Amount of catalyzate obtained (g) | Gas and losses (%) | Properties of catalyzate | | | Composition of gas (%) | |
|---|---|---|---|---|---|---|---|---|---|
| | | | | | $n_D^{20}$ | $d_4^{20}$ | Content of aromatics (% by volume) | $H_2$ | $C_nH_{2n+2}$ |
| 1 | $Pt-SiO_2$ | 152.6 | 142.0 | 6.9 | 1.4208 | 0.7220 | 20.0 | 93.7 | 6.2 |
| 2 | $Pd-SiO_2$ | 177.2 | 166.5 | 6.0 | 1.3930 | 0.6909 | 7 | 95.3 | 4.7 |
| 3 | $Rh-SiO_2$ | 113.0 | 93.0 | 18.0 | 1.3925 | 0.6904 | 5 | 35.0 | 65.0 |
| 4 | $Ru-SiO_2$ | 128.4 | 102.7 | 20 | 1.3890 | 0.6855 | 1 | 32.5 | 67.5 |

TABLE 2

Properties of the Light Fractions separated from the Catalyzates before the Chromatographic Separation of Aromatic Hydrocarbons

| No. | Catalyst | Boiling range (°C) | $n_D^{20}$ | $d_4^{20}$ | Amount (g) | Yield (% by weight on catalyzate) | Yield (% by weight on original heptane) |
|---|---|---|---|---|---|---|---|
| 1 | $Pt-SiO_2$ | 22–33• | 1.3545 | 0.6054 | 8.8 | 6.2 | 5.8 |
| | | 33–40•• | 1.3600 | 0.6288 | 10.5 | 7.4 | 6.0 |
| 2 | $Pd-SiO_2$ | 29–40 | 1.3560 | 0.6258 | 2.8 | 2.3 | 1.6 |

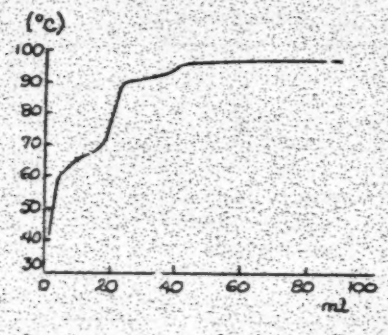



Fig. 2. Fractionation curve for the paraffin part of the heptane catalyzate obtained over a $Pt-SiO_2$ catalyst.

In the paraffin part of the heptane catalyzate obtained over $Pd-SiO_2$, the following hydrocarbons were found. In Fractions I and I' hexane 85–90% and 2- and 3-methylpentanes 5–10%. In Fraction II 2-methylhexane 60%, 2,4-dimethylpentane 23%, 2,3-dimethylpentane 12%, and 3,3-dimethylpentane 5%. In Fractions IV and V 2-methylhexane 55–60% and 3-methylhexane 45–40%. Fractions V' and V'' consisted of almost pure heptane.

In the catalyzate obtained in the experiment with $Rh-SiO_2$, Fractions I' and II were found to contain 2-methylhexane 25–30%, 3-methylhexane 20–25%, and heptane 55–45%. Fractions IV and V contained mainly unchanged heptane. The possibility of the presence of some branched C$_7$ paraffins in Fraction IV cannot be excluded. Fraction V' was almost pure heptane.

The following hydrocarbons were identified in the catalyzate obtained from heptane in presence of $Ru-SiO_2$: in Fractions I' and III, 2-methylhexane 25–30%, 3-methylhexane 20–25%, and heptane 55–45%. It is particularly noteworthy that Fraction V contained not only heptane, the content of which was 95%, but also 5% of methylcyclohexane, produced by the cyclization of heptane.

The fractional composition and properties of aromatic hydrocarbons isolated by adsorption on silica gel are given in Table 4.

The data in Table 4 show that the main aromatic product of the transformation of heptane is toluene. However, in the catalyzates obtained in experiments with Pt and Pd catalysts, small amounts of more complex benzene homologs were obtained (a 124–141° fraction, amounting to 1 g, and a 115–138° fraction, also 1 g). These hydrocarbons were submitted to Ullmann oxidation [7], and the resulting acids were separated by the method described by Moldavsky and coworkers [8]. The experimental results are given in Table 5.

• Bulk of it came over at 26–28° (754 mm).

•• Bulk of it came over at 33–35.6° (754 mm).

TABLE 2

Fractional Composition and Properties of the Paraffin Part of the Heptane Catalyzates

| Catalyst | Amount of catalyzate taken for fractionation (g) | Fraction No. | Properties of fractions: Boiling limits (°C) | $n_D^{20}$ | $d_4^{20}$ | Weight of fraction, (g) | Yield (%): on amount of catalyzate taken for fractionation | on weight of catalyzate obtained | on heptane taken for reaction |
|---|---|---|---|---|---|---|---|---|---|
| 0.5% Pt–$SiO_2$ | 64 | I | 40–45 | 1.3610 | 0.6290 | 0.6 | 0.9 | 0.4 | 0.4 |
| | | II | 45–60 | 1.3735 | 0.6561 | 2.6 | 4.1 | 1.9 | 1.7 |
| | | III | 60–65 | 1.3750 | 0.6620 | 2.6 | 4.1 | 1.9 | 1.7 |
| | | IV | 65–75 | 1.3805 | 0.6712 | 6.3 | 9.8 | 4.4 | 4.1 |
| | | V | 75–90 | 1.3905 | 0.6816 | 4.4 | 6.9 | 3.1 | 2.9 |
| | | VI | 90–95 | 1.3890 | 0.6851 | 10.8 | 16.9 | 7.6 | 7.1 |
| | | VII | 95–98 | 1.3882 | 0.6842 | 30.0 | 46.9 | 21.1 | 19.7 |
| | | VIII | 98–99 | 1.3885 | 0.6850 | 3.3 | 5.2 | 2.3 | 2.2 |
| | Losses | | – | – | – | 3.3 | 5.2 | – | – |
| 0.5% Pd–$SiO_2$ | 100 | I | 47–60 | 1.3625 | 0.6305 | 1.4 | 1.4 | 0.8 | 0.8 |
| | | II | 60–75 | 1.3799 | 0.6672 | 2.8 | 2.8 | 1.7 | 1.6 |
| | | III | 75–90 | 1.3885 | 0.6856 | 2.3 | 2.3 | 1.4 | 1.3 |
| | | IV | 90–95 | 1.3910 | 0.6886 | 11.1 | 11.1 | 6.6 | 6.2 |
| | | V | 95–96 | 1.3910 | 0.6868 | 2.5 | 2.5 | 1.5 | 1.4 |
| | | VI | 96–97 | 1.3885 | 0.6845 | 70.3 | 70.3 | 42.2 | 39.7 |
| | | VII | 97–98 | 1.3890 | 0.6852 | 4.8 | 4.8 | 2.9 | 2.7 |
| | Losses | | – | – | – | 4.8 | 4.8 | – | – |
| 0.5% Rh–$SiO_2$ | 66.8 | I | 65–80 | 1.3840 | – | 0.5 | 0.8 | 0.5 | 0.4 |
| | | II | 80–90 | 1.3875 | 0.6840 | 0.9 | 1.4 | 1.0 | 0.8 |
| | | III | 90–95 | 1.3887 | 0.6851 | 2.4 | 3.6 | 2.6 | 2.1 |
| | | IV | 95–96 | 1.3890 | 0.6849 | 5.3 | 7.9 | 5.7 | 4.7 |
| | | V | 96–96.5 | 1.3883 | 0.6845 | 52.9 | 79.2 | 56.9 | 46.9 |
| | Losses | VI | 96.5–101 | 1.3905 | 0.6860 | 3.7 | 5.5 | 4.0 | 3.3 |
| | | | – | – | – | 1.1 | 1.7 | – | – |
| 1% Ru–$SiO_2$ | 69 | I | 84.5–90 | – | – | 0.1 | 0.15 | 0.1 | 0.08 |
| | | II | 90–95 | 1.3890 | 0.6853 | 3.6 | 5.3 | 3.6 | 2.9 |
| | | III | 95–96 | 1.3885 | 0.6851 | 2.6 | 3.8 | 2.5 | 2.0 |
| | | IV | 96–97 | 1.3885 | 0.6842 | 58.1 | 84.2 | 56.5 | 45.2 |
| | | V | 97–100 | 1.3915 | 0.6879 | 3.7 | 5.4 | 3.6 | 2.9 |
| | | | 100–102.5 | 1.3925 | 0.6898 | | | | |
| | Losses | | – | – | – | 0.9 | 1.3 | – | – |

## DISCUSSION OF RESULTS

The investigation of the products of the reactions of heptane at 430° in presence of Pt, Pd, Rh, or Ru deposited on silica gel and of hydrogen at 20 atm in a continuous-flow system shows that some of the original heptane undergoes dehydrocyclization with formation of toluene:

$$CH_3-(CH_2)_5-CH_3 \longrightarrow \text{C}_6\text{H}_5\text{CH}_3 + 4H_2$$

The fact that aromatic hydrocarbons are formed over Pd and Rh catalysts is deserving of attention.

The researchers Kazansky and Frolikhov did not observe the formation of aromatic hydrocarbons when

octane was passed over palladized charcoal at atmospheric pressure and at a temperature of 300-310°. It follows that changes in the chemical nature of the carrier and in the experimental conditions can result in a radical change in the properties of the catalyst and in the way in which hydrocarbons behave in contact with it. The behavior of normal alkanes over a Rh catalyst has not been studied. As will be seen from the results of our experiments, under the conditions that we have used this catalyst behaves similarly to a palladium catalyst.

TABLE 4

Properties of Aromatic Hydrocarbons isolated from the Heptane Catalyzate

| Catalyst | Amount of substance taken for fractionation (g) | Fraction No. | Boiling limits (°C) | $n_D^{20}$ | $d_4^{20}$ | Amount of fraction (g) | Yield (% by weight) | | |
|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | on mixture taken for fractionation | on catalyzate | on original hydrocarbon |
| $Pt-SiO_2$ | 44.3 | I | 79.5–80 | 1.5005 | 0.8788 | 2.6 | 5.9 | 1.8 | 1.7 |
| | | II | 109.5–110.6 | 1.4965 | 0.8661 | 36.4 | 82.2 | 25.6 | 23.9 |
| | | III | 124–141 | 1.5000 | – | 1.0 | 2.2 | 0.71 | 0.7 |
| $Pd-SiO_2$ | 7.2 | I | 108–112 | 1.4930 | 0.8620 | 5.2 | 72.3 | 3.1 | 2.9 |
| | | II | 115–138 | 1.4960 | – | 1.0 | 14.0 | 0.6 | 0.6 |
| $Rh-SiO_2$ | 4.8 | I | 105–109.1 | 1.4930 | – | 0.5 | 10.5 | 0.5 | 0.45 |
| | | II | 109.1–110 | 1.4965 | 0.8664 | 4.0 | 84.0 | 4.3 | 3.5 |

TABLE 5

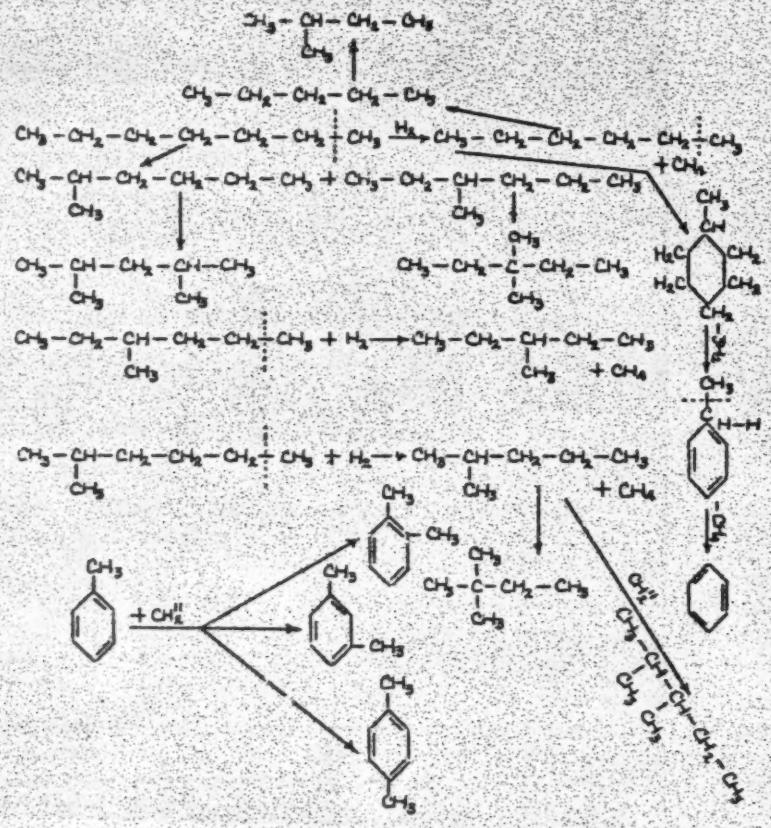
Properties of Carboxylic Acids obtained by the Oxidation of the 115-138° and 124-141° Aromatic Fractions obtained in Experiments with Palladized and Platinized Silica Gel respectively

| Catalyst | Acid | Amount of acid (g) | M.p. (°C) | Compound used for the identification of the acid |
|---|---|---|---|---|
| $Pd-SiO_2$ | Benzoic | 0.25 | 121 | The acid |
| | Phthalic | 0.09 | 131 | Phthalic anhydride |
| | Isophthalic | 0.11 | 62–63 | Methyl ester |
| | Terephthalic | 0.05 | 139–140 | Methyl ester |
| $Pt-SiO_2$ | Benzoic | 0.18 | 121 | The acid |
| | Phthalic | 0.12 | 131 | Phthalic anhydride |
| | Isophthalic | 0.098 | 63–64 | Methyl ester |
| | Terephthalic | 0.06 | 138–139 | Methyl ester |

The fact, which we are the first to observe, that methylcyclohexane (about 5%) is formed directly from heptane in presence of $Ru-SiO_2$, is of great interest. It shows that methylcyclohexane is formed intermediately in the catalytic dehydrocyclization of heptane. We shall endeavor to follow up this interesting observation in greater detail in further experimental investigations. Kazansky, Liberman, and Batuev [10] have already concluded, from a study of the products of the catalytic treatment of 3,3-dimethylhexane over platinized charcoal, that the aromatization of paraffins over platinum proceeds via the intermediate formation of six membered cycles; these authors showed that 1,1 dimethylcyclohexane was present in the reaction product.

We consider that xylenes are formed by the methylation of toluene by methylene radicals that arise under the conditions of the experiment, and that benzene results from the partial demethylation of toluene. Under our conditions, methylene radicals may arise, on the one hand, by the breakdown of heptane, and on the other, by the breakdown of the cyclohexane hydrocarbons that are formed under the given conditions, as was shown already in 1934 by Zelinsky and Shuikin [11].

The types of catalysis product obtained, and their great variety, indicate that heptane undergoes very far-reaching transformations in presence of the investigated metal catalysts applied on a silica gel carrier.



## SUMMARY


1. An investigation has been made of the reactions of heptane at 460° in a continuous flow system in presence of Ru, Rh, Pd, and Pt deposited on silica gel and of hydrogen at 20 atm. Ruthenium, rhodium, and palladium have been applied for the first time in the study of the transformations of heptane.

2. It has been shown that, under the given conditions, heptane undergoes far-reaching transformations in various directions; apart from toluene, benzene and xylenes were found among the aromatic products. In the paraffin part of the catalyzate, $C_5$–$C_7$ branched hydrocarbons were found.

3. An appreciable amount (about 5%) of methylcyclohexane was found among the products of the catalytic treatment of heptane over Ru-$SiO_2$. This fact indicates that the formation of a six-membered ring occurs as an intermediate stage in the dehydrocyclization of alkanes having a chain of six or more carbon atoms.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# REACTIONS OF INDIVIDUAL HYDROCARBONS IN CONTACT WITH NATURAL ALUMINOSILICATES

## COMMUNICATION 2. REACTIONS OF CYCLOHEXANE, METHYLCYCLOHEXANE, AND TOLUENE IN PRESENCE OF TROSHKOV CLAY

E. A. Timofeeva and N. I. Shuikin

As is well known, catalytic cracking has now assumed great importance in the petroleum industry. A study of undoubted interest in this connection is that of the behavior of individual hydrocarbons of different classes in contact with aluminosilicates.

There are data in the literature on the cracking of cycloalkanes in presence of synthetic aluminosilicate catalysts. Frost [1] considers that naphthenes undergo cracking in contact with aluminosilicates with formation of olefins, which, as a result of isomerization and decomposition, yield branched hydrocarbons. Bloch and Thomas [2] have studied the transformations of deca- and tetra-hydronaphthalenes in presence of a synthetic zirconia-alumina-silica catalyst at 400-500°, and they have shown the catalysis processes include dehydrogenation, isomerization, ring fission, and redistribution of hydrogen. Greensfelder and Voge [3] investigated the cracking of eleven naphthenes having 6-18 carbon atoms in contact with an aluminosilicate catalyst of composition $SiO_2$ 86.2%, $ZrO_2$ 9.4%, and $Al_2O_3$ 4.4% at 450-550°. These authors showed that the rate at which the cycloalkanes were broken down increased rapidly with increase in molecular weight and was independent of their structures. Thus, the degree of conversion increased from 7% for $C_6$ hydrocarbons to 79% for $C_{18}$ hydrocarbons.

Maslyansky and Berlin [4], who investigated the transformations of cyclohexane over a synthetic aluminosilicate at 515-560° at ordinary pressure, established that the breakdown of cyclohexane was mainly in the direction of the formation of gaseous products, among which hydrogen and methane hydrocarbons predominated. The isomerization of cyclohexane into methycylopentane occurred only to a slight extent. In experiments of the same investigators [5] with methylcyclohexane at 515° it was shown that, apart from toluene, the reaction products contained o-, m-, and p-xylenes, ethylbenzene, trimethylbenzene, and other aromatic hydrocarbons boiling above 170°. Among the products of the transformation of methylcyclohexane, dimethylcyclopentane and also paraffin and olefin hydrocarbons were found.

Hence, in the catalytic treatment of cycloalkanes in presence of synthetic aluminosilicate catalysts at atmospheric pressure, cracking, isomerization, alkylation, ring-fission, and dehydrogenation reactions occur. The degree of conversion of the cycloalkane depends on its molecular weight; the higher the molecular weight, the higher the degree of conversion of the cycloalkane. The fact that complex aromatic hydrocarbons (xylene, trimethylbenzene) are among the transformation products of cyclohexane and methylcyclohexane is of great interest.

Thomas, Hoekstra, and Prinkston [6] have investigated the cracking of ethylbenzene, cumene, butylbenzene, and commercial amylbenzene in presence of synthetic aluminosilicate catalysts at 400-500°. They found that, when the side chain contained three or more carbon atoms, it was readily split off in the catalysis process with formation of benzene. Ethylbenzene and toluene are more stable than the higher hydrocarbons mentioned above.

A study of the literature cited shows that, although the transformations of cycloalkanes and aromatic hydrocarbons in presence of synthetic aluminosilicates have received fairly detailed investigation, there are still problems that remain to be solved. These are associated with the complexity of the process, the determination of the order in which the reactions occur, and other matters relating to the mechanism of catalytic cracking.

In our work we have studied the behavior of cyclohexane and methylcyclohexane in contact with a natural aluminosilicate (activated Troshkov clay) with the object of determining the sequence of reactions occuring in the catalytic transformations of cycloalkanes. With the same object in view we have studied also the reactions of toluene under conditions similar to those of the reactions of methylcyclohexane. As a result of these investigations we have found definite regularities in the behavior of cycloalkanes in presence of a natural aluminosilicate, and have established that in these processes the alkylation reactions proceeding concurrently with the dehydrogenation of the

cycloalkanes are predominantly important. This investigation forms a continuation of our studies of the catalytic properties of Troshkov kaolin [7, 8, 9].

## EXPERIMENTAL

The pure hydrocarbons used in the investigation had the following properties:

| | B.p. (corrected, °C) | $n_D^{20}$ | $d_4^{20}$ |
|---|---|---|---|
| Cyclohexane | 80.7 | 1.4265 | 0.7787 |
| Methylcyclohexane | 100.3–100.8 | 1.4230 | 0.7699 |
| Toluene | 110.7 | 1.4960 | 0.8663 |

### Experimental Conditions and Analytical Procedure

The catalytic treatment was carried out at 450° and 500° at atmospheric pressure at a space velocity of 0.3 in a continuous-flow apparatus. The catalyst was prepared from activated Troshkov clay. The clay was activated with sulfuric acid. The chemical composition of the clay has been stated in a previous paper [7]. All of the experiments were carried out with the same portion of catalyst (volume 100 ml, weight 92.5 g, length of layer 44.0 cm, internal diameter of catalysis tube 20 mm).

After each series of experiments with a given hydrocarbon, the catalyst was regenerated by air oxidation at 500° for 4–5 hours. The amount of sulfonatable hydrocarbons was determined by absorption in 2% oleum, and iodine numbers were determined by the Margosches method [10]. The naphthene-paraffin part of the catalyzate was separated from aromatic and unsaturated hydrocarbons by an adsorption method. The compositions of some of the catalyzate fractions were investigated by the Raman spectrum method.

### Contact-catalysis Reactions of Cyclohexane

The transformations of cyclohexane were studied at 450° and 500°. The hydrocarbon was passed in 50-ml (38.9 g) portions. The properties of the resulting catalyzates are given in Table 1 (the results of typical experiments are given).

TABLE 1

Properties of Cyclohexane Catalyzates

| Temperature of experiment (°C) | Yield of catalyzate (%) | Yield of gas (liters at N.T.P.) | Properties of Catalyzate | | | | |
|---|---|---|---|---|---|---|---|
| | | | $n_D^{20}$ | $d_4^{20}$ | Sulfonatables (% by volume) | Iodine number | Unsaturated hydrocarbons (% by weight) |
| 450 | 97.5 | 0.500 | 1.4260 | 0.7767 | 2.7 | 0.3 | 0.1 |
| 500 | 95.1 | 1.507 | 1.4265 | 0.7748 | 5.2 | 5.8 | 1.9 |

Analysis of gas

| | Temperature 450° | 500° |
|---|---|---|
| Unsaturateds | 9.6% | 8.7% |
| Hydrogen | 90.1% | 87.0% |
| Paraffins | 0.3% | 4.3% |

The more detailed investigation of the 450° and 500° catalyzates showed that they were approximately the same in composition. The results of the investigation of the 450° catalyzate will therefore not be given here.

Investigation of the 500° Catalyzate. The combined catalyzate from six experiments, amounting to 213 g, was separated into three parts by distillation through a 28-plate column. The properties of these fractions are given in Table 2.

Part (12.6 g) of the catalyzate fraction boiling over the range 57.0–80.4° was mixed with decane (as a "cushion") and redistilled through the same column. It yielded 8.2 g of almost pure cyclohexane ($n_D^{20}$ 1.4260; $d_4^{20}$ 0.7780) and 4.0 g of a fraction boiling at 65.6–78.4°(corrected) and having $n_D^{20}$ 1.4185; $d_4^{20}$ 0.7571. Investigation of this fraction by the Raman spectrum method showed that, apart from cyclohexane, it contained benzene, methylcyclopentane, and un-

saturated hydrocarbons (probably mainly cis-2-hexene).

TABLE 2

Properties of Fractions of Cyclohexane Catalyzates

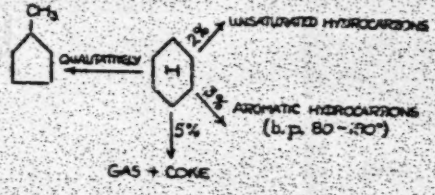
| Fraction No. | Boiling limits (°C, corrected) | Amount (g) | Properties of fractions | | | |
|---|---|---|---|---|---|---|
| | | | $n_D^{20}$ | $d_4^{20}$ | Sulfonatables (%) | Iodine number |
| I | 57.0–80.4 | 15.3 | 1.4220 | 0.7655 | 11.0 | 30.6 |
| II | 80.4–80.8 | 164.2 | 1.4263 | 0.7780 | 0.0 | 0.0 |
| III | 80.8–210.0 | 30.2 | 1.4410 | 0.7960 | 22.5 | 2.8 |
| Residue | | 0.3 | 1.5240 | – | – | – |

The third fraction of the catalyzate (see Table 2) was freed from aromatic hydrocarbons by passage through silica gel. The resulting dearomatized fraction (29.0 g) was distilled over sodium and came over in the range 79.8–81.0° (corrected); it had $n_D^{20}$ 1.4270 and $d_4^{20}$ 0.7782. It corresponded in properties to cyclohexane.

The mixture of aromatic with some unsaturated hydrocarbons boiled over the range 110–190° and had $n_D^{20}$ 1.5170. In view of the very small amount of this fraction (0.8 g), it was not investigated in detail.

Hence, in the catalytic treatment of cyclohexane at 500° in presence of Troshkov clay, some aromatic hydrocarbons (benzene and its homologs), some unsaturated hydrocarbons, and a very small amount of methylcyclopentane were formed. No benzene was found in the 450° catalysis experiments.

The transformations of cyclohexane at 500° in contact with activated Troshkov clay may be represented diagrammatically as follows:




The overall degree of conversion of cyclohexane was 11-12%.

Contact Catalysis Reactions of Methylcyclohexane

Methylcyclohexane was passed over the same catalyst in 100 ml (77.0 g) portions. The properties of the resulting catalyzates are given in Table 3.

TABLE 3

Properties of Methylcyclohexane Catalyzates

| Expt. No. | Temperature of experiment (°C) | Yield of catalyzate (%) | Yield of gas (liters at N.T.P.) | Properties of catalyzate | | | |
|---|---|---|---|---|---|---|---|
| | | | | $n_D^{20}$ | $d_4^{20}$ | Sulfonatables (% by volume) | Iodine number |
| 1 | 450 | 94.8 | 1.462 | 1.4195 | 0.7661 | 8.5 | 5.1 |
| 2 | 450 | 98.3 | 1.426 | 1.4200 | | | |
| 3 | 500 | 89.3 | 3.373 | 1.4228 | 0.7695 | 15.0 | 11.1 |
| 4 | 500 | 86.8 | 3.290 | 1.4232 | | | |

Analysis of gas

| Temperature | 450 (Expt. No. 1) | 500° (Expt. No. 3) |
|---|---|---|
| Unsaturateds | 15.6% | 18.2% |
| Hydrogen | 42.6% | 35.7% |
| Paraffins | 41.8% | 46.1% |

The results of the investigations of the 450° methylcyclohexane catalyzate will not be given, as it does not differ essentially in composition from the 500° catalyzate.

Investigation of the 500° Catalyzate. A portion (57.7 g) of the combined catalyzate from experiments carried out at 500° was separated by adsorption on silica gel into naphthene-paraffin (iodine number 25.0) parts. The curve for the fractionation of the naphthene-paraffin part of the catalyzate at 760 mm is given in Fig. 1. The properties of the fractions obtained are given in Table 4.

Owing to the very small amount available, the first fraction was not investigated. Raman spectrum analysis of the second fraction showed that it contained unchanged methylcyclohexane, heptane, 2-methylhexane, and 3-methylhexane. In the third fraction, 1,2-dimethylcyclopentane was found, and its presence is confirmed by the properties of this fraction (see the fractionation curve in Fig. 1). The fourth and fifth fractions consisted almost entirely of unchanged methylcyclohexane.

TABLE 4

Properties of Fractions of the Combined 500° Methylcyclohexane Catalyzate

| Fraction No. | Boiling limits (° C) | Amount (g) | $n_D^{20}$ | $d_4^{20}$ | Aniline point (° C) |
|---|---|---|---|---|---|
| I | 72 - 86.4 | 0.5 | 1.4080 | — | — |
| II | 86.4 - 98.0 | 2.9 | 1.4140 | 0.7533 | 50.8 |
| III | 98.0 - 100.2 | 8.5 | 1.4220 | 0.7700 | 42.7 |
| IV | 100.2 - 100.9 | 32.3 | 1.4228 | 0.7698 | — |
| V | 100.9 - 102.6 | 2.5 | 1.4228 | 0.7699 | 38.8 |
| Residue | | 0.2 | 1.4310 | — | — |

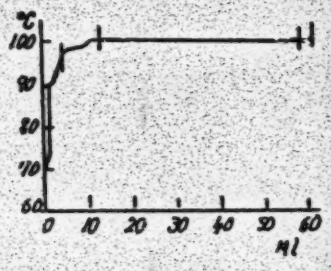
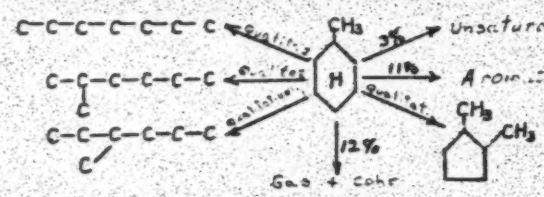



Fig. 1. Fractionation curve for the naphthene-paraffin part of the methylcyclohexane catalyzate.

The mixture (6.6 g) of aromatic and unsaturated hydrocarbons separated by adsorption boiled over the range 98-202° and had $n_D^{20}$ and $d_4^{20}$ 0.8357. A narrower fraction (1.8 g) was distilled from this mixture over the range 105-150° ($n_D^{20}$ 1.4900) and was oxidized with alkaline permanganate. From the oxidation products, benzoic acid (m.p. 121°) was isolated as such, and isophthalic and terephthalic acids were isolated in the form of their methyl esters (m.p. 63° and 141° respectively). These results confirm the presence of toluene, m-xylene, and p-xylene in the fraction oxidized.

Hence, in the catalytic treatment of methylcyclohexane in presence of Troshkov clay, toluene, xylenes, and more complex benzene homologs are formed; also, isomerization occurs, with contraction of the ring from six-membe to five-membered. It is probable that, apart from these changes, cleavage of the 1,2-dimethylcyclpentane ring occur with formation of heptane and its branched isomers. In the catalytic reaction a small amount (3%) of unsaturated hydrocarbons is also formed.

The transformations of methylcyclohexane at 500° in presence of activated Troshkov clay may be represented diagrammatically as follows:




Degree of conversion 30 - 32%.

A comparison of the behavior of cyclohexane with that of methylcyclohexane under the conditions of catalytic treatment in presence of Troshkov clay shows that cyclohexane is much less reactive than methylcyclohexane. Thus, at 500°, the degree of conversion of the former is no more than 11-12%, while the degree of conversion of the latter under the same conditions attains 30 - 32%. Under these conditions cyclohexane yields 3% of aromatic hydrocarbons and methylcyclohexane yields 11%. No paraffins were found in the cyclohexane catalyzates, whereas in the transformation products of methylcyclohexane, heptane, 2-methylhexane, and 3-methylhexane were found.

Heptane and 3-methylhexane were formed probably as a result of the opening of the ring of 1,2-dimethylcyclopentane, which we found to be present and which was itself the product of the isomerization of methylcyclohexane with contraction of the ring. 2-Methylhexane could have been formed by the isomerization of heptane.

## Contact-catalysis Reactions of Toluene

Toluene (100 ml) was passed over the same catalyst at 500° in 50-ml (43.3 g) portions. The properties of the resulting catalyzates are given in Table 5.

TABLE 5

Properties of Toluene Catalyzates

| Expt. No. | Yield (% by weight) | Yield of gas (liters at N.T.P.) | $n_D^{20}$ | $d_4^{20}$ |
|---|---|---|---|---|
| 1 | 96.8 | 0.308 | 1.4960 | 0.8660 |
| 2 | 97.0 | 0.495 | 1.4960 | |

TABLE 6

Properties of Fractions of Toluene Catalyzates

| Fraction No. | Boiling limits (°C) | Amount (% by weight) | $n_D^{20}$ | $d_4^{20}$ |
|---|---|---|---|---|
| I | 78.8–83.5 | 1.1 | 1.4998 | – |
| II | 83.5–111.8 | 96.5 | 1.4970 | 0.8670 |
| III | 111.8–157.8 | 2.0 | 1.5190 | – |
| Residue . . . . . | | 0.4 | 1.5300 | – |

The catalyzates contained traces of unsaturated hydrocarbons. The combined catalyzate (82.3 g) was fractionated through a 20-plate column into three fractions. The fractionation curve is shown in Fig. 2. The properties of the fractions are given in Table 6.

Hence, in the catalytic treatment of toluene in presence of activated Troshkov clay, about 1% of benzene and more than 2% of aromatic hydrocarbons boiling in the range 111.8–157.8° were obtained, 96.5% of the toluene remained unchanged.

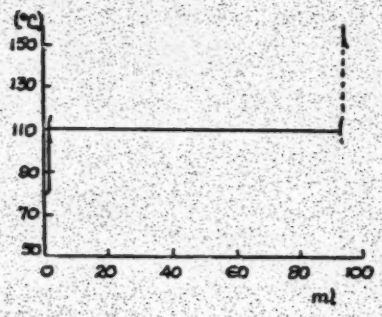



Fig. 2. Fractionation curve for the toluene catalyzate

A comparison of these results with those obtained for the transformations of methylcyclohexane results in some clarification of the sequence of reactions occurring in the catalytic treatment of methylcyclohexane. We have found that, as would be expected, toluene is stable under the given catalysis conditions: almost 97% of it remained unchanged. If the dehydrogenation of the methylcyclohexane were the primary reaction, then the bulk of the aromatic hydrocarbons formed would consist of toluene. Actually, however, the amount of toluene formed in the treatment of methylcyclohexane is much less than the amount of more complex benzene homologs. It must be supposed that under the given conditions, not only cracking and isomerization of the six-membered cycle occur, but also its alkylation by breakdown products; it is the subsequent dehydrogenation of the resulting higher cyclonexane homologs that is responsible for the formation of the corresponding aromatic hydrocarbons. However, the possibility is not excluded that, in the investigated catalytic reactions of cyclohexane and methylcyclohexane, benzene and toluene formed by the dehydrogenation of these cycloalkanes may be alkylated by the same cracking products.

## SUMMARY

1. A study has been made of the transformations undergone by cyclohexane, methylcyclohexane, and toluene at 450° and at 500° in contact with activated Troshkov clay.

2. It has been shown that the degree of conversion of cycloalkanes increases with rise in molecular weight, at 500°, it is 11–12% for cyclohexane and 30–32% for methylcyclohexane.

3. In the products obtained by the catalytic treatment of cyclohexane, not only benzene has been found, but also its homologs, together with methylcyclopentane and unsaturated hydrocarbons.

4. Under the same conditions, methylcyclohexane yields toluene, m- and p-xylenes, and other benzene homologs. Other products are dimethylcyclopentane, paraffins – probably formed by fission of the dimethylcyclopentane ring – and unsaturated hydrocarbons.

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* See Consultants Bureau translation, page 469.
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# REACTION OF THE COMPONENTS OF SKELETAL NICKEL WITH INORGANIC OXIDANTS

L. Kh. Freidlin and K. G. Rudneva

An important characteristic of a skeletal nickel catalyst (Raney nickel) is its high chemical activity. Bougault and coworkers [1] have shown that, unlike the nickel catalyst prepared by reduction of nickelous oxide, a skeletal nickel catalyst forms a solid amalgam with mercury. Aubry [2] found that, like nickel saturated cathodically with hydrogen [3], skeletal nickel displaces copper from copper sulfate and copper acetate solutions, and it reacts readily also with sulfite, thiosulfate, and selenite solutions, and it reduces iodates, chlorates, bromates, permanganates, ferricyanides, and other inorganic oxidizing agents. Nickel prepared by reduction of nickelous oxide does not react with oxidizing agents under similar conditions. In all of these cases the reducing action of a skeletal nickel catalyst is attributed solely to the sorbed hydrogen.

The results that we have now obtained show that the reducing effect does not arise exclusively from one source: not only the hydrogen, but also the metal is involved in the oxidation-reduction process. According to the character of this process, either the hydrogen sorbed in the nickel is the main reactant, or both the hydrogen and the metal react simultaneously with the oxidizing agent.

## EXPERIMENTAL

### Experimental Procedure and Conditions

The reaction was carried out in a glass hydrogenation flask fitted with an outlet tube and a filter. The skeletal nickel was prepared by the leaching of a 50% Ni-Al alloy with 20% caustic soda at 100°, and it was kept under water. The flask was blown out with nitrogen, and a spoonful of the nickel paste was washed into it with water. The oxidizing agent was added, the taps were closed, and the flask was shaken mechanically at room temperature. The metal was separated from the liquid, and its residual content of hydrogen was determined. The filtrate was analyzed for residual oxidizing agent.

### Reaction of Skeletal Nickel Catalyst with Potassium Permanganate

When a solution of potassium permanganate was added to a suspension of nickel in water, decolorization was rapid. The reaction was so rapid that it was not possible to make the kinetic measurements necessary to determine which of the components reacted first, the hydrogen or the nickel. It is probable that both reacted simultaneously. We have, in fact, shown in a special experiment that nickel freed from hydrogen with the aid of p-benzoquinone [4] is also able to reduce potassium permanganate rapidly at room temperature.

### Reaction of Skeletal Nickel Catalyst with Sodium Iodate

A spoonful of nickel (1 g) was suspended in 10 ml of water, and the oxidizing agent was added, as a 0.6 N solution, in an amount (0.6083 g) that was in excess of the equivalent of the hydrogen contained in the catalyst. The mixture was shaken, and the shaker was stopped at short intervals of time for the taking of samples of the solution, in which residual iodate was determined iodometrically.

As will be seen from Table 1 and Fig. 1, the kinetics of the reaction of skeletal nickel catalyst with sodium iodate have the same character in their early stages as the kinetics of the reaction with p-benzoquinone [4]. During the first few minutes the reaction proceeds at an enormous rate, after which the rate falls sharply and then continues to fall. The reaction does not stop, however, even after 76 minutes from the beginning of the experiment. Thus, after the mixture had stood for two days, some more (about 0.06 g) of the oxidizing agent had been consumed. The total amount of sodium iodate consumed in this experiment was 0.5483 g, corresponding to 186.2 ml of hydrogen. The catalyst was then washed free from oxidant (tested with acidified potassium iodide solution), and was treated for one hour at 60° with 0.8014 g of p-benzoquinone in dioxane in order to determine the hydrogen remaining in the nickel after treatment with sodium iodate [4]. The determination of the hydroquinone formed showed that 39.3 ml of hydrogen remained in the nickel after the iodate treatment (Expt. No. 1, Table 2). These results give the total amount of hydrogen per 1 g of catalyst as 225.5 ml, which is about 50 ml more than the amount of hydrogen, as determined with the aid of p-benzoquinone only. It follows that after long contact sodium iodate reacts not only with hydrogen contained in the nickel, but also with the metal itself.

TABLE 1

Kinetics of the Reaction of Sodium Iodate with Skeletal Nickel Catalyst (1 g) at 20°

| Test No. | Time from beginning of experiment (minutes) | Residual sodium iodate found in solution (g) | Amount of sodium iodate that reacted between the tests (g) | Amount of hydrogen (or its equivalent) removed from catalyst (ml) |
|---|---|---|---|---|
| 1 | 3 | 0.2226 | 0.3857 | 131.0 |
| 2 | 8 | 0.1882 | 0.0344 | 11.6 |
| 3 | 12 | 0.1772 | 0.0110 | 3.8 |
| 4 | 16 | 0.1621 | 0.0151 | 5.1 |
| 5 | 21 | 0.1517 | 0.0104 | 3.5 |
| 6 | 27 | 0.1435 | 0.0082 | 2.8 |
| 7 | 33 | 0.1358 | 0.0077 | 2.6 |
| 8 | 44 | 0.1343 | 0.0015 | 0.5 |
| 9 | 76 | 0.1188 | 0.0155 | 5.3 |
| 10 | After standing for two days | 0.0600 | 0.0588 | 20.0 |
| | Total amount of hydrogen removed. . . | | | 186.2 ml |

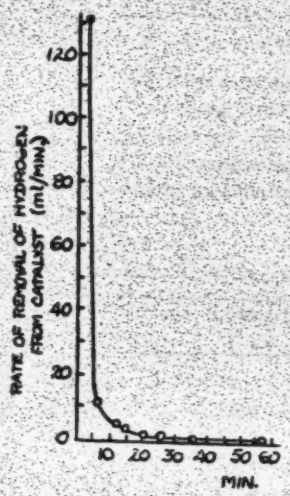


Fig. 1. Kinetics of the reaction of 1 g of skeletal nickel catalyst with sodium iodate at 20°.

TABLE 2

Hydrogen Removal from 1 g of Skeletal Nickel Catalyst with the aid of Sodium Iodate

| Expt. No. | Experimental conditions | | Amount consumed | | Hydrogen removed (ml) | | | Amount of nickel oxidized (%) |
|---|---|---|---|---|---|---|---|---|
| | Temperature (°C) | Time of contact (minutes) | sodium iodate (g) | p-benzoquinone (g) | with the aid of sodium iodate | with the aid of p-benzoquinone | altogether | |
| 1 | 20 | 76 | 0.4895 | -- | 166.2 | — | 166.2 | — |
| | | two days | 0.5483 | 0.1888 | 186.2 | 39.3 | 225.5 | 12.2 |
| 2 | 20 | 30 | 0.4125 | 0.2798 | 139.9 | 62.2 | 202.1 | 7.0 |
| 3 | 20 | 30 | 0.3067 | 0.3740 | 103.2 | 77.7 | 180.9 | 1.3 |
| 4 | 60 | 86 | 0.5482 | 0.1458 | 187.0 | 30.2 | 217.2 | 10.7 |

TABLE 3

Kinetics of the Reaction of Skeletal Nickel Catalyst (1 g) with an Alkaline Solution of Iodine at 20° (initial amount of iodine 2.8153 g)

| Test No. | Time from beginning of experiment (minutes) | Duration of shaking between tests (minutes) | Amount of residual iodine found (g) | Amount of iodine that reacted between the tests (g) | Amount of hydrogen removed from the catalyst (ml) |
|---|---|---|---|---|---|
| 1 | 3 | 3 | 1.3617 | 1.4534 | 128.0 |
| 2 | 7 | 3 | 1.2956 | 0.0661 | 5.8 |
| 3 | 11 | 3 | 1.2057 | 0.0899 | 7.9 |
| 4 | 16 | 3 | 1.1620 | 0.0437 | 3.8 |
| 5 | 20 | 3 | 1.1407 | 0.0213 | 1.9 |
| 6 | 26 | 5 | 1.1208 | 0.0199 | 1.8 |
| 7 | 32 | 5 | 1.0974 | 0.0234 | 2.0 |
| 8 | 43 | 10 | 1.0566 | 0.0408 | 3.6 |
| 9 | 54 | 10 | 1.0368 | 0.0198 | 1.7 |
| 10 | 77 | 20 | 1.0368 | 0 | 0 |
| | | | Total amount of hydrogen removed. . . . | | 156.5 ml |

Two further experiments were then carried out, and in these a spoonful of skeletal nickel catalyst was first treated with an insufficient amount of sodium iodate and then exhaustively with p-benzoquinone. It was considered that, if the sodium iodate reacted at first only with sorbed hydrogen but later also with metal, the total amount of hydrogen determined by the successive treatment of the nickel with sodium iodate and p-benzoquinone would be approximately equal to the amount determined by benzoquinone only, so long as an insufficient amount of sodium iodate was used.

The results confirmed this supposition. For example (Expt. No. 2, Table 2), after treatment of the nickel with 0.4125 g of sodium iodate - which corresponds to 139.9 ml of hydrogen (80% of the hydrogen contained in the metal) - a further 62.2 ml was determined as hydroquinone. The total amount of hydrogen in 1 g of nickel (202.1 ml), so determined, was only 26 ml more than the amount of hydrogen found in the nickel with the aid of p-benzoquinone. When a still smaller amount (0.3067 g) of oxidant was used (Expt. No. 3, Table 2), corresponding to 103.2 ml of hydrogen (60% of the hydrogen contained in the nickel), the further amount determined from the amount of hydroquinone formed was 77.7 ml, i.e. 180.9 ml of hydrogen altogether in 1 g of nickel. The amount found with the aid of p-benzoquinone was precisely the same. It follows, therefore, that at the beginning of the process the sodium iodate does, in fact, react only with the hydrogen. When the greater part (60-70%) of the hydrogen has reacted, slow reaction of the oxidant with the metal begins to occur concurrently with the main reaction. As in hydrogen removal with p-benzoquinone, the character of the kinetics of the process does not change when the temperature is raised from 20° to 60°.

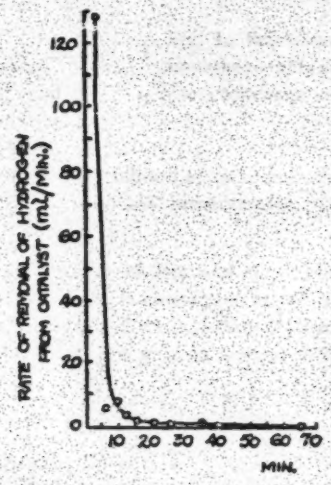


Fig. 2. Kinetics of the reaction of 1 g of skeletal nickel catalyst with an alkaline solution of iodine at 20°.

The behavior of this oxidant was greatly different from that of potassium permanganate. In the sodium iodate process it was possible to distinguish kinetically between the initial stage, in which reaction is with hydrogen only, and the subsequent stage, in which reaction with metal also occurs. In Expts. No. 2 and 3 (Table 2), in which insufficient amounts of sodium iodate were used at 20°, the amounts of metal oxidized were about 7% and 1.3% respectively, but at 60°, with an excess of oxidant (Expt. No. 4, Table 2), the amount oxidized was 11%.

We obtained similar results in experiments on the kinetics of the removal of hydrogen from another sample of nickel with an alkaline solution of iodine at 20°. The solution was prepared by addition of 5% caustic soda solution to 0.5 N iodine until it was just decolorized. In an experiment with a 4% excess (with respect to the hydrogen in the nickel) of oxidant, almost the same amount of hydrogen was found (136.9 ml) as in an experiment with a 60% excess (156.5 ml), (Table 3). It will be seen from Fig. 2 that the kinetics of the reaction of skeletal nickel with an alkaline solution of iodine are exactly the same in character as the kinetics of the benzoquinone reaction. The inactive nickel obtained by freeing the metal from hydrogen with the aid of p-benzoquinone, does not react with an alkaline solution of iodine.

## Reaction of Skeletal Nickel Catalyst with Oxygen

Bougault, Cattelain, and Chabrier [1] treated a suspension of 20 g of skeletal nickel catalyst suspended in 100 ml of water with air at room temperature for 30 days. Test samples of the catalyst were taken at intervals and analyzed for total and sorbed hydrogen. Total hydrogen was determined by dissolution of the sample in hydrochloric acid. Simultaneously, the nickel content of the solution was determined. The difference between the total hydrogen and the volume of hydrogen displaced from the acid by nickel was taken as sorbed hydrogen. It was thus shown that 1 g of the nickel contained about 140 ml of hydrogen. It was found that the total hydrogen content of the test samples fell more rapidly with time than the volume of sorbed hydrogen, from which the authors concluded that, in the course of the treatment of the catalyst with oxygen, removal of hydrogen was accompanied by oxidation of metal. Their results were qualitative.

Our new procedure has enabled us to study the rate of the process and to determine the proportions in which the oxygen is distributed between the hydrogen and the metal. When an aqueous suspension of skeletal nickel catalyst (1 g) was shaken at room temperature with oxygen in a hydrogenation flask, 101 ml of oxygen was consumed, which exceeds the amount required for the oxidation of the hydrogen contained in the nickel by 13 ml. Fig. 3

shows the rate of absorption of oxygen by the catalyst. It will be seen that absorption is most rapid in the first few minutes, and gradually falls with time. The kinetics of the reaction with oxygen differ greatly from those of the benzoquinone and sodium iodate reactions. The oxygen reaction is considerably slower, particularly in the early stages. It is probable that oxygen also is sorbed by nickel, but does not form a continuous film that would interfere with the reaction of the residual hydrogen in the metal with benzoquinone. This is in accord with the fact that, even after a 10-12-hour treatment of skeletal nickel catalyst with air under water, no nickelous oxide lines could be detected in the X-ray diagram [5].

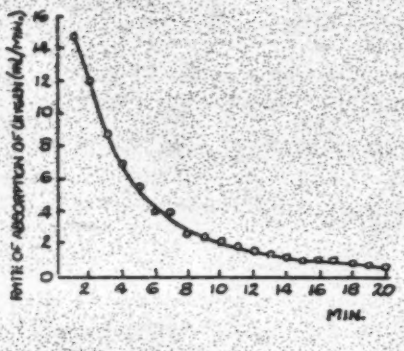


Fig. 3. Kinetics of the absorption of oxygen by 1 g of skeletal nickel catalyst at 20°.

Another sample of nickel (2 g) containing 378 ml of hydrogen was treated in the same way with an excess of oxygen, and 191 ml of oxygen was absorbed. It was then found, from the amount of hydroquinone formed in the catalyst, that there was 121 ml of residual hydrogen. Hence, only 257 (378−121) ml of hydrogen had reacted with oxygen; the remaining 63 $\left(191-\frac{257}{2}\right)$ ml of oxygen was probably consumed in the formation of a film on the nickel.

A catalyst from which hydrogen had been removed completely by means of p-benzoquinone did not react with oxygen at room temperature and pressure, from which it may be inferred that the hydrogen sorbed in the nickel determines not only the catalytic activity of skeletal nickel, but also its high chemical activity.

## Reactivation of Catalyst that has been Deactivated with Inorganic Oxidants

As would be expected, skeletal nickel loses the whole of its catalytic activity when treated exhaustively with oxidizing agent (potassium permanganate, oxygen, sodium iodate, and an alkaline solution of iodine). This behavior may be explained not only by the complete removal of hydrogen from the catalyst, but also by the formation of a film having a blocking action on its surface. We have previously shown [6] that a catalyst that has been deactivated by means of p-benzoquinone will acquire the power of absorbing hydrogen when heated to only 60° (i.e. its metal-hydrogen surface will be partially regenerated) and will then catalyze hydrogenation at room temperature. Since it is probable that a surface film of nickelous oxide will not be reduced by hydrogen at 60°, it would not be expected that the same reactivation effect would be obtained by a similar treatment of skeletal nickel that has been deactivated with various oxidizing agents. We have obtained results that confirm this supposition (Table 4). The experiments were carried out as follows: 1 g of active skeletal nickel was treated with the oxidizing agent in an atmosphere of nitrogen, carefully freed from oxidant by washing with water and then alcohol, and shaken while being saturated with hydrogen at 60°. In order to determine the activity of the catalyst, 0.2495 g of phenyl vinyl ether was added in 10 ml of alcohol and the rate of absorption of hydrogen was measured at 20°.

TABLE 4

Reactivation of Catalyst that has been Deactivated with Oxidizing Agents

| Oxidizing agent | Consumption of oxidizing agent per gram of catalyst, expressed as ml of hydrogen removed | Saturation of catalyst, after its treatment with the oxidizing agent, with hydrogen at 60° | | Activity of the catalyst during each of the first four minutes of the hydrogenation of phenyl vinyl ether expressed as rate of absorption of hydrogen at 20° (ml/min) |
|---|---|---|---|---|
| | | hydrogen consumed (ml) | time for saturation (minutes) | |
| p-Benzoquinone [4] | 176.0 | 60 | 60 | 4.3− 1.6−1.1−1.1 |
| $O_2$ | 159.0 | 12.4 | 20 | 0.6− 0.4−0.4−0.4 |
| $NaIO_3$ | 192.1 | 0 | 45 | 0−0−0−0 |
| $NaIO_3$ | 68.8 | 16.8 | 35 | 2.8−2.8−2.8−2.6 |

When skeletal nickel was exhaustively oxidized with oxygen and then shaken for 20 minutes at 60° while being treated with hydrogen, 12.4 ml of hydrogen was absorbed, and the catalyst had only a very slight activity in the hydrogenation reaction. The results of this experiment are in accord with the conclusion reached earlier, namely that the oxygen, while oxidizing the hydrogen sorbed in the nickel simultaneously forms a film on the surface of the nickel which does not prevent the nickel from again absorbing hydrogen.

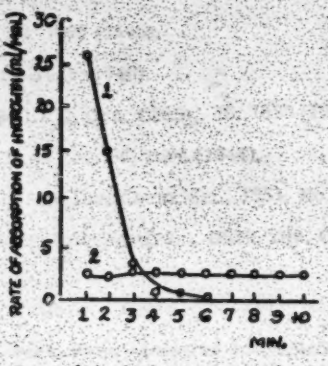


Fig. 4. Rate of the hydrogenation of 0.2495 g of phenyl vinyl ether in alcohol at 20°: 1 - in presence of unoxidized catalyst; 2 - in presence of catalyst oxidized with $NaIO_3$ and then treated with hydrogen.

When nickel that had been treated with an excess of sodium iodate was shaken in presence of hydrogen for 45 minutes at 60°, no hydrogen was absorbed and the nickel did not catalyze the hydrogenation of phenyl vinyl ether or of eugenol. When a catalyst (1 g) that had been treated with an insufficient amount of sodium iodate (equivalent to 68.8 ml of hydrogen) was shaken in presence of hydrogen for 35 minutes at 60°, 16.8 ml of hydrogen was absorbed, and the product had an appreciable activity for the hydrogenation of phenyl vinyl ether (Fig. 4). Confirmation is thus provided for our view that sodium iodate reacts in the first place with sorbed hydrogen, and later also with the metal, so that, during the oxidation of skeletal nickel with an excess of sodium iodate, not only removal of hydrogen occurs, but also the formation of an oxide film.

## SUMMARY

1. A study has been made of the relative reactivities of the nickel and hydrogen components of a skeletal catalyst in their reaction with inorganic oxidizing agents at room temperature.

2. When the catalyst is treated with potassium permanganate, both the nickel and the hydrogen take part in the process.

3. Kinetic and analytical studies show that sodium iodate reacts primarily with the sorbed hydrogen, but reaction occurs also with the metal.

4. The rate of reaction of skeletal nickel with oxygen is much lower by a factor of 5-6 than that of its reaction with p-benzoquinone or sodium iodate. About two-thirds of the oxygen consumed reacts with hydrogen, and about one-third with the metal.

5. The results show that the high reducing power of skeletal nickel is due to the presence of sorbed hydrogen and to the high degree of dispersion of the metal itself.

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# MACROMOLECULAR COMPOUNDS

## COMMUNICATION 67. PROPERTIES OF POLYESTERS FORMED BY DICARBOXYLIC ACIDS WITH SOME POLYMETHYLENE GLYCOLS

V. V. Korshak, S. V. Vinogradova, and E. S. Vlasova

The relationship between the properties of polyesters and their structures has not yet received detailed consideration in the literature in spite of its great scientific importance as an essential part of the general problem of the relationship between the properties of macromolecular compounds and their structures. Only isolated attempts have been made to establish this relationship. Thus, Hill and Walker [1] attempted to show that in a homologous series of polyesters of general formula $[-O(CH_2)_nOCOCH_2(CH_2)_mCH_2CO]_x$, in which n + m had the values 14, 16, 18, and 22, the melting points varied according to a smooth curve. It follows from their results that the melting points of polyesters derived from even acids do not depend on the distribution of methylene groups between the acid and the glycol, but only on the total number of methylene groups in the repeating unit. The limited experimental data at the disposal of these authors did not permit them to make wider generalizations.

A second relevant investigation is that carried out by us on polyesters formed by 1,20-eicosanediol with the homologous series of dicarboxylic acids from oxalic to sebacic [2, 3]. It was found that the melting points of the polyesters vary according to a zig-zag line, the melting points of polyesters of dicarboxylic acids having even numbers of carbon atoms (even acids) being higher than those of dicarboxylic acids having odd numbers of carbon atoms (odd acids). An odd acid forms a polyester of lower melting point than those of the polyesters of the two neighboring even acids. When we consider the polyesters of even acids separately, it is found that there is a minimum in the curve for variation of melting point with the number of carbon atoms. On the contrary, the melting point curve for polyesters of odd acids does not show a minimum, but rises smoothly. It is not possible to make use of the data in the literature on the melting points of the individual polyesters, partly because of the gaps in these data, but mainly because of the great variation that is often found between the values given by different authors [4]. Reliable data can be obtained only by preparing all of the esters under identical conditions, and it was with this object that the present investigation was carried out.

## EXPERIMENTAL

### Experimental Procedure and Results

We prepared the polyesters formed by ethylene glycol, 1,6 hexanediol, and 1,10-decanediol with the following dicarboxylic acids: oxalic, malonic, succinic, glutaric, adipic, pimelic, suberic, azelaic, and sebacic. Oxalic and malonic acids were used in the form of their diethyl esters, and the remaining acids were applied in the free state. The experimental procedure for the polyesterification reaction has been described in detail previously [2]. An equimolecular mixture of glycol and dicarboxylic acid was heated in an atmosphere of nitrogen for ten hours at 170° and for two hours at 190°, and was then heated at a residual pressure of 2 mm Hg for two hours at 190°, for two hours at 210°, and for ten hours at 250°. The mixtures of the diethyl esters of oxalic and malonic acids with glycols were heated in a current of nitrogen for six hours at 100°, for two hours at 120°, for four hours at 140°, and for eight hours at 170°, and then under reduced pressure for five hours at 170°, for six hours at 200°, for one hour at 210°, for 90 minutes at 220°, for two hours at 230°, and for one hour at 240°. The molecular weights of the resulting polyesters were determined from the viscosities of 0.5% benzene solutions, and their melting points and solubilities in benzene and alcohol were also determined. The results are given in Table 1.

As will be seen from the data in Fig. 1, the melting points and solubilities of polyesters formed by ethylene glycol, 1,6-hexanediol, and 1,10-decanediol with dicarboxylic acids bear definite relationships not only to the total number of carbon atoms in the acid molecule, but also to the odd or even character of this number. These relationships are in general similar to those found for the polyesters of 1,20-eicosanediol, investigated previously [2,3], but certain features are more clearly expressed.

Let us examine in greater detail the dependence, first of the melting point, and then of the solubility, on the structure of the polyester, i.e., on the structures of the acid and glycol. It should be noted first of all that in the series

of polyesters formed by ethylene glycol, 1,6-hexanediol, and 1,10-decanediol, as in the series of 1,20-eicosanediol polyesters that we have already described, polyesters of even acids have higher melting points than polyesters of odd acids. This can be readily seen from Figures 1, 2, and 3, which show the dependence of the melting points of the polyesters of the respective glycols on the number of carbon atoms in the molecule of the dicarboxylic acid.

TABLE 1

Properties of Polyesters formed by Dicarboxylic Acids with some Polymethylene Glycols

| Polyester | No. of atoms in repeating unit | M.p. (°C) | Solubility of polyester (g/liter of solvent) | | Molecular weight |
|---|---|---|---|---|---|
| | | | in benzene | in alcohol | |
| Polyethylene oxalate | 6 | 159–161 | 2.26 | — | — |
| Polyethylene malonate | 7 | −22—18 | 3.18 | — | 1150 |
| Polyethylene succinate | 8 | 102–103 | 5.52 | — | 3760 |
| Polyethylene glutarate | 9 | −19—12 | 180.45 | — | 1220 |
| Polyethylene adipate | 10 | 47–52 | 182.84 | 11.5 | 2220 |
| Polyethylene pimelate | 11 | 25–29 | 181.15 | — | 2620 |
| Polyethylene suberate | 12 | 63–65 | 184.08 | — | 1370 |
| Polyethylene azelate | 13 | 44–47 | 181.84 | 17.4 | 2400 |
| Polyethylene sebacate | 14 | 72–74 | 169.80 | 9.7 | 1180 |
| Polyhexamethylene oxalate | 10 | 70–72 | 186.12 | 3.06 | 3290 |
| Polyhexamethylene malonate | 11 | −48—42 | 184.81 | 9.22 | 2270 |
| Polyhexamethylene succinate | 12 | 52–55 | 171.12 | 5.3 | 3300 |
| Polyhexamethylene glutarate | 13 | 28–34 | 174.08 | 20.0 | 2180 |
| Polyhexamethylene adipate | 14 | 55–58 | 189.92 | 8.86 | 3080 |
| Polyhexamethylene pimelate | 15 | 52–55 | 177.48 | 14.0 | 4650 |
| Polyhexamethylene suberate | 16 | 61–65 | 172.92 | 3.9 | 3960 |
| Polyhexamethylene azelate | 17 | 52–55 | 210.44 | 12.45 | 2520 |
| Polyhexamethylene sebacate | 18 | 65–68 | 181.16 | 4.90 | 3510 |
| Polydecamethylene oxalate | 14 | 76–79 | 165.56 | — | 2620 |
| Polydecamethylene malonate | 15 | 29–34 | 159.08 | — | 2310 |
| Polydecamethylene succinate | 16 | 71–73 | 163.36 | — | 4370 |
| Polydecamethylene glutarate | 17 | 55–58 | 171.16 | 1.5 | 3800 |
| Polydecamethylene adipate | 18 | 70–74 | — | — | 3340 |
| Polydecamethylene pimelate | 19 | 63–66 | — | — | 3150 |
| Polydecamethylene suberate | 20 | 70–75 | — | — | 3880 |
| Polydecamethylene azelate | 21 | 67–69 | — | 3.2 | 4450 |
| Polydecamethylene sebacate | 22 | 71–76 | 164.60 | 1.15 | 3270 |

Fig. 1 shows that the melting points of polyesters formedby ethylene glycol with dicarboxylic acids lie on a zig-zag curve. When however, the variation in melting point is considered separately for polyesters of even and odd dicarboxylic acids, two comparatively smooth curves are obtained, which are shown by the broken lines in Fig. 1. It must be stressed, however, that the courses of the two curves are greatly different, i.e. increase in the number of carbon atoms in the dicarboxylic acid affects the melting point differently in the two cases.

In the series of odd-acid polyesters a continuously rising melting point curve is obtained, whereas in the series of even-acid polyesters the melting point curve has a minimum at a point corresponding to the polyester derived from adipic acid.

The greatest change in melting point from one polyester to the next is that for the polyesters of oxalic and malonic acids; it amounts to 181°. The difference for the polyesters of malonic and succinic acids is 124°; for succinic and glutaric polyesters it is 121°, and as we proceed further the difference diminishes. In the series of polyesters derived from even acids the greatest difference in melting point is that between the oxalic and succinic polyesters, i.e. 57°; the difference then falls, and for the suberic and sebacic polyesters it is only 10°. In the series of odd-acid polyesters, the differences in melting point are lower, the greatest difference being that for the glutaric and pimelic polyesters, namely 44°.

An examination of the melting point curve for polyesters of 1,6-hexanediol (Fig. 2) reveals a similar general picture, but the absolute values of the melting point differences are lower, and the minimum melting point in the

series of polyesters derived from even acids is that of the succinic polyester. The difference of the melting points of the oxalic and malonic polyesters of 1,6-hexanediol is 118°, i.e. less than in the ethylene glycol series.

The dependence of the melting points of polyesters formed by 1,10-decanediol with dicarboxylic acids on the number of carbon atoms in the acid is shown in Fig. 3.

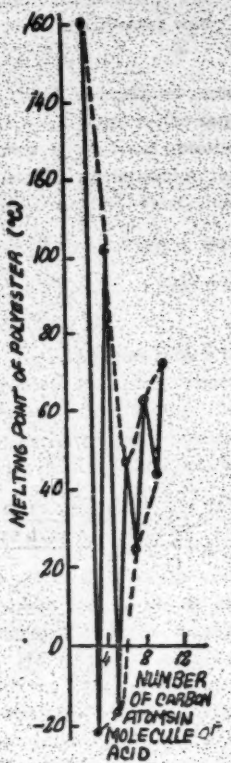


Fig. 1. Dependence of the melting points of polyesters of ethylene glycol on the number of carbon atoms in the molecule of dicarboxylic acid.

Fig. 3 shows that the greatest difference in melting points (between the oxalic and malonic polyesters) is only 47°. The variation in the melting points of the even-acid polyesters is only small, and the minimum melting point, which is that of adipic acid, is only slightly less than that of succeeding acids. In this respect the picture is similar to that which we found previously for the polyesters of 1,20-eicosanediol [2, 3].

For the characterization of intermolecular forces in polyesters, their solubilities in organic solvents are of great interest. Table 1 gives the solubilities of the polyesters in benzene and in alcohol at 20°. The solubility in benzene was determined for almost all of the polyesters, but the solubility in alcohol was determined only for a few.

It will be readily seen that the ethylene glycol polyesters of oxalic, malonic, and succinic acids have very low solubilities in benzene, and contrast greatly with the remaining polyesters, which have solubilities of higher than 160 g per liter. Polyhexamethylene azalaate is particularly soluble, being, in fact, the most soluble of all of the polyesters investigated.

Systematic determinations of alcohol-solubility were made only for the 1,6-hexanediol polyesters. The absolute solubilities are clearly much less, ranging from 3.06 to 20 g per liter, as compared with benzene-solubilities ranging to 210.44 g per liter. It is noteworthy also that, whereas the solubility in benzene does not depend to an appreciable extent on whether the polyester is derived from an even or an odd acid, the alcohol-solubilities of odd-acid polyesters are appreciably higher than those of even-acid polyesters. Thus, the solubilities of polyesters derived from even acids vary over the range 3.06-8.86 g per liter, whereas the solubilities of odd-acid polyesters vary from 9.22 to 20.0 g per liter, i.e. are appreciably higher. In Fig. 4 the dependence of the alcohol-solubilities of 1,6-hexanediol polyesters on the number of carbon atoms in the molecule of the dicarboxylic acid is illustrated graphically.

It will be readily seen that we again have a zig-zag curve, but the peaks now correspond to odd-acid polyesters, and the lower points to even-acid polyesters. This relationship is to be observed also for the other polyesters that we have synthesized, i.e. those derived from ethylene glycol and 1,10-decanediol: the azelaic polyesters were found to be more soluble than the adipic and sebacic polyesters.

Fig. 5 shows the dependence of the alcohol-solubilities of adipic, azelaic, and sebacic polyesters on the number of carbon atoms in the glycol molecule, and it will be seen that the azelaic polyesters are the most soluble, being considerably superior in this respect to the adipic and sebacic polyesters.

## DISCUSSION OF RESULTS

The properties of the polyesters that we have investigated are determined by factors such as the number of methylene groups in the repeating unit, which changes as we pass from one dicarboxylic acid to the next in the homologous series, and the relative dispositions of bonds, which change as we pass from an even to an odd acid.

To understand the variations in the melting points and solubilities of the polyesters it is necessary to consider the fact that their macromolecules contain such groups as $-CH_2-$, $-CO-$, and $-O-$, which affect the melting points of compounds containing them in different ways. In previous papers [2, 3] we have given detailed consideration to the effects of these groups on the melting points of organic compounds containing them, and we shall confine ourselves here to a short summary of this material.

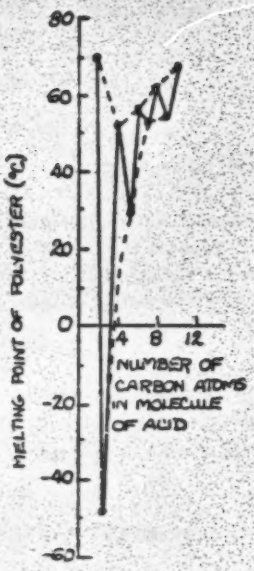


Fig. 2. Dependence of the melting points of polyesters of 1,6-hexanediol on the number of carbon atoms in the molecule of the dicarboxylic acid.

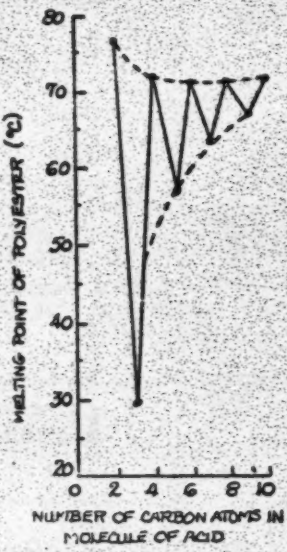


Fig. 3. Dependence of the melting points of polyesters of 1,10-decanediol on the number of carbon atoms in the molecule of the dicarboxylic acid.

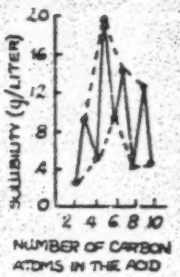


Fig. 4. Dependence of the alcohol-solubilities of 1,6-hexanediol polyesters on the number of carbon atoms in the molecule of the dicarboxylic acid.

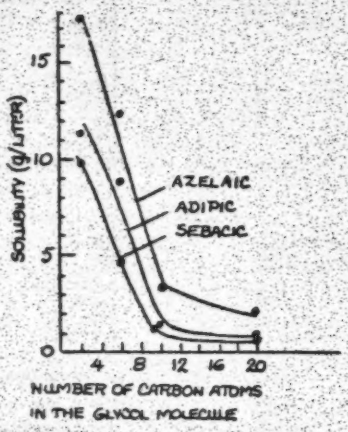


Fig. 5. Dependence of the alcohol-solubilities of polyesters of dicarboxylic acids on the number of carbon atoms in the glycol molecule.

The introduction of an ether linkage into a hydrocarbon molecule increase the flexibility of the chain because of the greater ease of rotation about the linkage $-C-O-C$, and therefore favors a lowering of melting point. The introduction of a carbonyl group into a hydrocarbon molecule results in a rise in melting point due to increase in the rigidity of the chain, as can be readily seen in the case of aliphatic ketones, whose melting points are higher than those of the corresponding hydrocarbons.

In polyesters, therefore, there are two opposing factors that affect their melting points: the presence of oxygen linkages, associated with a lowering of melting point in comparison with that of polyethylene; and the presence of linkages through carbonyl, associated with the raising of the melting point. To these factors must be added the evenness factor, the effect of which is particularly marked when a series of polyesters derived from even acids is compared with the corresponding series derived from odd acids. The evenness factor has not yet been completely explained, but, as we have previously pointed out [2, 3], its functioning probably depends on polar effects in the dicarboxylic acid molecules. This question will be examined in greater detail in a future paper.

If we neglect the effect of the evenness factor, then we can explain satisfactorily the courses of the melting point curves for the even-acid polyesters and for the odd-acid polyesters, which are represented by the broken lines in Figures 2, 3, and 4. For example, the anomalously high melting points and low solubilities of the first polyesters of ethylene glycol, polyethylene oxalate and polyethylene succinate can be understood when the fact that there are high proportions of carbonyl groups in these polyesters is taken into account. When the proportion of carbonyl groups is reduced, the melting point falls, and polyethylene adipate melts at 47-52°. As the proportion of carbonyl groups falls, the proportion of ester oxygen linkages also falls and the proportion of methylene groups rises, and these changes should result in a rise in melting point. In the series of even-acid polyesters derived from ethylene glycol the minimum point occurs at polyethylene adipate, which melts at 47°.

For polyesters derived from odd acids the picture is much different, owing to the operation of the evenness factor. This apparently results in a great increase in the effect of the ether linkages, so that polyesters derived from odd dicarboxylic acids melt at much lower temperatures. Increase in the content of methylene groups neutralizes this effect, so that the melting point rises as we pass from the lower odd-acid polyesters to the higher homologs.

TABLE 2

Variation in the Contents of Carbonyl Groups, Ester Oxygens, and Methylene Groups in the Series of Ethylene Glycol Polyesters.

| Polyester | Number of atoms in chain of residue | | | Content in polyester (% by weight) | | |
|---|---|---|---|---|---|---|
| | glycol | acid | repeating unit | carbonyl groups | ester oxygens | methylene groups |
| Polyethylene oxalate | 3 | 3 | 6 | 48.27 | 27.58 | 24.14 |
| Polyethylene malonate | 3 | 4 | 7 | 43.08 | 24.61 | 32.31 |
| Polyethylene succinate | 3 | 5 | 8 | 38.88 | 22.22 | 38.90 |
| Polyethylene glutarate | 3 | 6 | 9 | 35.44 | 20.25 | 44.31 |
| Polyethylene adipate | 3 | 7 | 10 | 32.56 | 18.60 | 51.16 |
| Polyethylene pimelate | 3 | 8 | 11 | 30.10 | 17.20 | 52.70 |
| Polyethylene suberate | 3 | 9 | 12 | 28.00 | 16.00 | 56.00 |
| Polyethylene azelate | 3 | 10 | 13 | 26.17 | 14.95 | 58.78 |
| Polyethylene sebacate | 3 | 11 | 14 | 24.56 | 14.03 | 61.41 |

The variation in the contents of carbonyl groups, ester oxygens, and methylene groups, expressed in percentage by weight, is shown in Table 2, from which it can be seen that these contents change in a very smooth fashion, without any jumps, from one polyester to another, so that it is impossible to explain the great and sudden variations in melting point solely on the basis of the variations in the contents of carbonyl groups, ester oxygens, and methylene groups. A determining part is played here by the evenness factor, the nature of which will be considered in a later paper.

If we now return to an examination of our results, it will be readily seen that the view suggested by Hill and Walker's work [1], namely, that the melting point of a polyester depends only on the total proportion of methylene groups in the molecule and not on the way in which these methylene groups are distributed, i.e. on whether they are in the acid residue or the glycol residue, is incorrect in the general case. In illustration of this point, the melting points of polyesters having the same number of atoms in the chain of the repeating unit are compared in Table 3.

Among the ten pairs of polyesters given in Table 3, some are of the even-acid series and some are of the odd-acid series, but in no case do the melting points agree sufficiently closely to provide support for the above-mentioned hypothesis. On the contrary, the data for the ten pairs of polyesters given in Table 3 indicate that the melting points of polyesters are determined not only by the number of atoms in the chain of the repeating unit, or the number of methylene groups in the repeating unit, but also by the way in which these methylene groups are distributed between the acid and glycol residues, as can be readily seen from the examples cited.

Our results enable us to examine the dependence of the melting points of polyesters of various dicarboxylic acids on the number of carbon atoms in the glycol. This relationship is shown in Fig. 6, from which it can be seen that the melting point curves of the polyesters of oxalic, malonic, and succinic acids have minima, corresponding to the polyesters formed with 1,6-hexanediol. It is clear that for these polyesters the effect of the ester oxygen linkage attains its maximum, resulting in a maximum lowering of melting point; its effect then becomes weaker owing to the increase in the number of methylene groups, and the melting point rises. There are no minima in the curves of the polyesters of the other acids, and the melting point rises continuously as the number of methylene groups in the glycol increases. Finally, it should be noted that Fig. 6 again illustrates quite clearly that even-acid polyesters have higher melting points than odd-acid polyesters.

TABLE 3

Melting points of Polyesters having the Same Number of Atoms in the Chain of the Repeating Unit

| Total number of atoms in the chain of the repeating unit | Number of atoms in the chain of the residue | | Polyester | M.p.(°C) |
|---|---|---|---|---|
| | glycol | acid | | |
| 10 | 3 | 7 | Polyethylene adipate | 47 – 52 |
| 10 | 7 | 3 | Polyhexamethylene oxalate | 70 – 72 |
| 11 | 3 | 8 | Polyethylene pimelate | 25 – 29 |
| 11 | 7 | 4 | Polyhexamethylene malonate | –46 – –42 |
| 12 | 3 | 9 | Polyethylene suberate | 63 – 65 |
| 12 | 7 | 5 | Polyhexamethylene succinate | 52 – 55 |
| 13 | 3 | 10 | Polyethylene azelate | 44 – 47 |
| 13 | 7 | 6 | Polyhexamethylene glutarate | 28 – 34 |
| 14 | 3 | 11 | Polyethylene sebacate | 72 – 74 |
| 14 | 7 | 7 | Polyhexamethylene adipate | 55 – 58 |
| 14 | 11 | 3 | Polydecamethylene oxalate | 76 – 79 |
| 15 | 7 | 8 | Polyhexamethylene pimelate | 52 – 55 |
| 15 | 11 | 4 | Polydecamethylene malonate | 29 – 34 |
| 16 | 7 | 9 | Polyhexamethylene suberate | 61 – 65 |
| 16 | 11 | 5 | Polydecamethylene succinate | 71 – 73 |
| 17 | 7 | 10 | Polyhexamethylene azelate | 52 – 55 |
| 17 | 11 | 6 | Polydecamethylene glutarate | 55 – 58 |
| 18 | 7 | 11 | Polyhexamethylene sebacate | 65 – 68 |
| 18 | 11 | 7 | Polydecamethylene adipate | 70 – 74 |

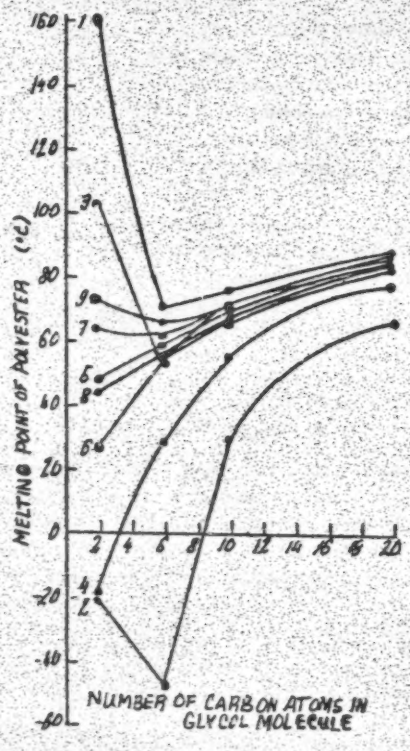


Fig. 6. Variation of the melting points of the polyesters of the following acids: 1-oxalic; 2 malonic; 3-succinic; 4-glutaric; 5-adipic; 6-pimelic; 7-suberic; 8-azelaic; 9-sebacic

## SUMMARY


1. The polyesters formed by ethylene glycol, 1,6-hexanediol, and 1,10-decanediol with the following dicarboxylic acids have been prepared under identical conditions: oxalic, malonic, succinic, glutaric, adipic, pimelic, suberic, azelaic, and sebacic acids.

2. Polyesters derived from dicarboxylic acids having even numbers of carbon atoms have higher melting points than the neighboring pairs of odd-acid polyesters.

3. The solubilities of the polyesters in benzene and alcohol have been determined, and it has been found that the polyesters of the odd dicarboxylic acids have the higher solubilities in alcohol.

4. An explanation has been advanced for the way in which the properties of the polyesters depend on their structures.

5. It has been established that the melting points of polyesters depend not only on the number of methylene groups in the repeating unit, but also on their distribution within the unit.


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## MACROMOLECULAR COMPOUNDS

# COMMUNICATION 68. EFFECT ON THE PROPERTIES OF POLYESTERS OF THE INTRODUCTION OF ETHER OXYGENS AND SIDE CHAINS

V. V. Korshak, S. V. Vinogradova, and E. S. Vlasova

In the preceding communication we have examined the dependence of the properties of polyesters on their structures as illustrated by the behavior of the polyesters formed by ethylene glycol, 1,6-hexanediol, and 1,10-decanediol with dicarboxylic acids, namely, oxalic, malonic, succinic, glutaric, adipic, pimelic, suberic, azelaic, and sebacic acids [1]. These polyesters were prepared under identical conditions, so that we were able to compare their properties with the object of relating them to the structures of the polymers. It was found that polyesters of dicarboxylic acids having even numbers of carbon atoms in their molecules (even acids) have higher melting points than the polyesters of odd dicarboxylic acids. Similarly, the alcohol-solubilities of the former were found to be lower than those of the latter.

We considered that the variations in melting point in these series of polyesters could be explained by taking into account the effects of oxygen linkages, carbonyl groups, and methylene groups occurring in the polyester chain in various proportions and in various arrangements. With the object of establishing the part played by each of these groups in determining the properties of the polyester, we have now synthesized polyesters from glycols containing ether linkages, and we have also prepared polyesters having methyl side groups.

## EXPERIMENTAL

### Experimental Procedure and Results

The method of preparing the polyesters was the same as that described previously [1, 2]. The glycols used were diethylene glycol, triethylene glycol, and 1,2-propanediol, and the dicarboxylic acids were the members of the homologous series from oxalic to sebacic.

The properties of the resulting polyesters are given in the table. Their melting points and solubilities in benzene and alcohol were determined, and also their molecular weights from their viscosities in benzene solution.

## DISCUSSION OF RESULTS

An examination of the tabulated properties of the polyesters permits some inferences to be made concerning the relationship between their properties and their structures. The validity of such inferences made on the basis of a comparison of these properties is increased by the fact that the polyesters were prepared under identical conditions and do not vary greatly in molecular weight.

Fig. 1 shows the curve for the variation of the melting points of polyesters prepared from diethylene glycol. It has the zig-zag form already found for the polyesters of some polymethylene glycols [1, 2], the melting points of the polyesters of even acids being higher than those of the neighboring polyesters of odd acids. The analogy cannot be carried further, however, for a comparison with the graph for the melting points of polyesters derived from polymethylene glycols immediately reveals essential differences. In the first place, the greatest differences in melting point are found for the polyesters of sebacic, azelaic, suberic, and pimelic acids, i.e. of the higher acids, whereas for the polyesters derived from polymethylene glycols, the greatest differences were found for the lower members, i.e. the polyesters of oxalic, malonic, and succinic acids. In the second place, the melting point curve of the odd-acid polyesters falls as we pass to those derived from acids containing more methylene groups, whereas the corresponding curve for the odd-acid polyesters of polymethylene glycols rises. It is clear that in the polyesters of diethylene glycol the effect of the methylene groups is completely overcome by the evenness effect and the effect of the oxygen linkages. The melting point curve for the even-acid polyesters has a very sharp minimum at the point corresponding to the polyester of adipic acid, and the rise that follows is much steeper than that on the curve for the polyesters of polymethylene glycols. It is clear that in this region the effect of the accumulation of methylene

groups is already making itself felt, and this results in a rise in melting point, as already observed for the polyesters of polymethylene glycols, the melting points of which always rise for the same reason, as we pass to the polyesters of the higher acids.

TABLE

Properties of Polyesters formed by Dicarboxylic Acids with Certain Glycols

| Polyester | Number of atoms in chain of repeating unit | M.p. (°C) | Solubility of polyester (g in 1 liter of solvent) in | | Viscosimetric molecular weight |
|---|---|---|---|---|---|
| | | | benzene | alcohol | |
| Poly[2,2'-oxydiethyl oxalate] | 9 | 5 – 10 | 3.2 | – | 2930 |
| Poly[2,2'-oxydiethyl malonate] | 10 | – 18 – – 11 | 17.4 | – | 2100 |
| Poly[2,2'-oxydiethyl succinate] | 11 | – 11 – – 8 | 166.0 | – | 2400 |
| Poly[2,2'-oxydiethyl glutarate] | 12 | – 30 – – 22 | 184.4 | – | 2440 |
| Poly[2,2'-oxydiethyl adipate] | 13 | – 29 – – 24 | 177.8 | 11.3 | 3780 |
| Poly[2,2'-oxydiethyl pimelate] | 14 | – 32 – – 26 | 162.2 | – | 3640 |
| Poly[2,2'-oxydiethyl suberate] | 15 | 28 – 35 | 160.0 | – | 3240 |
| Poly[2,2'-oxydiethyl azelate] | 16 | – 36 – – 31 | 185.1 | 19.0 | 2840 |
| Poly[2,2'-oxydiethyl sebacate] | 17 | 44 – 46 | 195.8 | 28.2 | 2080 |
| Poly[2,2'-(ethylenedioxy)diethyl oxalate] | 12 | – 14 – – 10 | 9.1 | – | 3660 |
| Poly[2,2'-(ethylenedioxy)diethyl malonate] | 13 | – 34 – – 28 | 22.8 | – | 3160 |
| Poly[2,2'-(ethylenedioxy)diethyl succinate] | 14 | – 24 – – 18 | 160.2 | – | 2240 |
| Poly[2,2'-(ethylenedioxy)diethyl glutarate] | 15 | – 36 – – 28 | 195.5 | – | 2580 |
| Poly[2,2'-(ethylenedioxy)diethyl adipate] | 16 | – 39 – – 30 | 90.8 | 20.6 | 2650 |
| Poly[2,2'-(ethylenedioxy)diethyl pimelate] | 17 | – 42 – – 37 | 195.5 | – | 3180 |
| Poly[2,2'-(ethylenedioxy)diethyl suberate] | 18 | – 41 – – 36 | 20.1 | – | 2820 |
| Poly[2,2'-(ethylenedioxy)diethyl azelate] | 19 | – 43 – – 40 | 184.4 | – | 2160 |
| Poly[2,2'-(ethylenedioxy)diethyl sebacate] | 20 | 28 – 33 | 186.8 | 29.9 | 2450 |
| Polypropylene succinate | 8 | – 2 – 0 | 182.9 | – | 1295 |
| Polypropylene glutarate | 9 | – 25 – – 18 | 182.3 | – | 1790 |
| Polypropylene adipate | 10 | – 25 – – 20 | 187.4 | 33.4 | 1130 |
| Polypropylene pimelate | 11 | – 37 – – 30 | 189.4 | – | 1630 |
| Polypropylene suberate | 12 | – 41 – – 34 | 185.0 | – | 1120 |
| Polypropylene azelate | 13 | – 46 – – 38 | 180.2 | 28.9 | 1300 |
| Polypropylene sebacate | 14 | – 34 – – 26 | 179.9 | 10.3 | 1480 |

The picture is somewhat different for the polyesters derived from triethylene glycol and dicarboxylic acids, as can be seen from Fig. 2, in which the melting point curve for the polyesters of triethylene glycol is given.

In this series the zig-zag form of the curve for the dependence of the melting point on the number of carbon atoms in the molecule of the acid is not completely maintained for the middle members, i.e. the polyesters of glutaric, adipic, and pimelic acids, so that the curve has a smooth section.

The melting point curve for the odd-acid polyesters falls continuously, like the corresponding curve for the polyesters of diethylene glycol. The curve for the even-acid polyesters is also very similar to the corresponding diethylene glycol curve, and its minimum corresponds to the polyester of pimelic acid. There is then a sharp rise in melting point as we pass to the polyester of sebacic acid, which may be an indication that the effect of the methylene groups is beginning to make itself felt. For the polyesters of diethylene glycol this effect begins to appear clearly at the point corresponding to suberic acid. It may therefore be stated that the addition of another ether oxygen to the molecule of the glycol neutralizes the effect of two methylene groups.

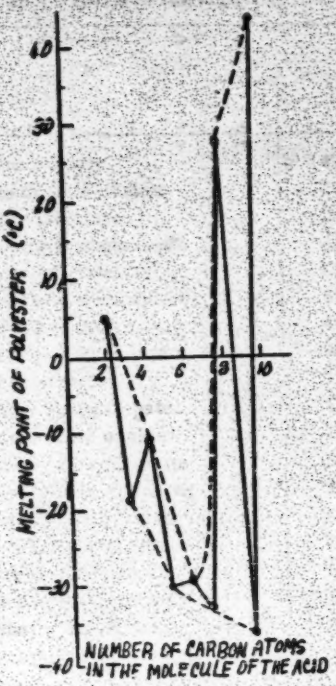


Fig. 1. Dependence of the melting points of polyesters of diethylene glycol on the number of carbon atoms in the molecule of the dicarboxylic acid.

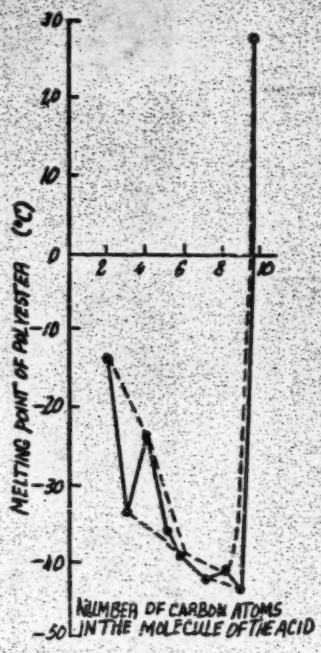


Fig. 2. Dependence of the melting points of polyesters of triethylene glycol on the number of carbon atoms in the molecule of the dicarboxylic acid.

It should be noted also that the polyesters of triethylene glycol have lower melting points than the corresponding polyesters of diethylene glycol. This evidently results from the effect of the second ether linkage, and it is analogous to the effect of the introduction of the first ether oxygen, for the melting points of the polyesters of ethylene glycol are higher than those of the polyesters of diethylene glycol, the difference being particularly great for the polyesters of even dicarboxylic acids.

It may be supposed that further increases in the number of ether linkages in the glycol will result in further smoothing of the melting point curve, so that it will finally become a smooth line. Thus, for tetraethylene glycol, and still more for pentaethylene glycol, we may expect the complete obliteration of the effect arising from an even number of carbon atoms in the acid. It may therefore be concluded quite definitely that the evenness factor and the effect of ether linkages are directly opposed to one another. The evenness factor is conducive to the formation of an ordered arrangement of macromolecules in the solid phase, whereas ether linkages facilitate the creation of a state of disorder, increasing the mobility of the macromolecules and making them less rigid, so that they no longer tend to form an ordered arrangement with respect to each other.

For the complete characterization of the properties of polyesters derived from diethylene and triethylene glycols it should be noted also that their benzene- and alcohol-solubilities, which are given in the table, are greatly different, like those of the polyesters of polymethylene glycols. The solubilities in benzene are considerably higher than those in alcohol. Also, the polyesters of oxalic and malonic acids are much less soluble than those of the other dicarboxylic acids, which have benzene-solubilities of more than 160 g per liter, with the exception of the polyesters formed by triethylene glycol with adipic and suberic acids, which are of somewhat lower solubility. The alcohol-solubilities of the polyesters rise as the number of methylene groups in the dicarboxylic acid increases, the solubilities of the polyesters formed by diethylene glycol with adipic, azelaic, and sebacic acids, for example, being 11.3, 19.0, and 28.2 g per liter respectively.

The introduction of methyl side groups into polymer molecule should have an appreciable effect on the properties of the substance. The table gives the melting points of the polyesters formed by 1,2-propanediol with dicarboxylic acids of the homologous series from succinic to sebacic. It will be seen that they are all liquids, the melting points being below 0°.

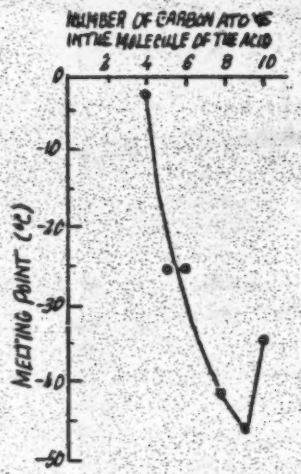


Fig. 3. Dependence of the melting points of polyesters of 1,2-propanediol on the number of carbon atoms in the molecule of the dicarboxylic acid.

Fig. 3 shows the curve for the dependence of the melting points of polyesters of 1,2-propanediol on the number of carbon atoms in the molecule of the dicarboxylic acid.

It will be seen from Fig. 3 that the melting points of the polyesters of 1,2-propanediol lie on a smooth curve having a minimum corresponding to the polyester of azelaic acid, the melting point of which (-45°) is lower than those of the other polyesters.

Hence, the accumulation of methylene groups in the dicarboxylic acid, up to the number of seven, is accompanied by a lowering of the melting point of the polyester, and only with sebacic acid, which has eight methylene groups, does a rise in melting point begin. Another peculiar feature of the melting point curve of polyesters of 1,2-propanediol is its smooth form, without the zig-zags that are so characteristic of the curves for the polyesters of ethylene glycol and other polymethylene glycols.

In the polyesters of 1,2-propanediol, the evenness factor has evidently been completely neutralized, and there are therefore no marked differences in the melting points of polyesters of even and odd dicarboxylic acids. The methylene side group has an effect similiar to that of an ether linkage in the molecule of the glycol, as seen in the polyesters of triethylene glycol, discussed above. The polyesters formed by triethylene glycol with the series of dicarboxylic acids from succinic to suberic inclusively also did not show effects attributable to the evenness factor, and their melting points fall on a smooth curve.

In this respect the introduction of methyl side groups is still more effective, since all of the polyesters of 1,2-propanediol, from the succinic to the azelaic polyester, have melting points that fall on a smooth curve. The great effectiveness of the methyl side group as an internal plasticizer is shown also by the fact that all of the polyesters that we have prepared from 1,2-propanediol are liquids, whereas only two of the polyesters of ethylene glycol were liquids at room temperature - the glutaric and malonic polyesters - the remainder being solids.

The powerful plasticizing effect of the methyl side group in polyesters of 1,2-propanediol is shown also by the fall in melting point that occurs as the number of methylene groups in the dicarboxylic acid molecule increases until we reach azelaic acid. Only when sebacic acid is reached does the curve rise, and increase in the number of methylene groups in the dicarboxylic acid begins to be accompanied by a corresponding rise in the melting point of the polyester.

We have made solubility determinations on the polyesters of 1,2-propanediol, and the results are given in the table. It will be seen from these data that the solubility of the investigated polyesters (of dicarboxylic acids from succinic to sebacic) is almost constant at about 184 g per liter. The alcohol-solubility is much lower and varies from 10.3 g per liter for polypropylene sebacate to 33.4 g per liter for polypropylene adipate, i.e. falls as the length of the methylene chain of the dicarboxylic acid increases.

In conclusion we may point out that the results of our investigations on the polyesters of diethylene glycol, triethylene glycol, and 1,2-propanediol show that the presence of an ether linkage or a methyl side group in these polyesters has a great effect on their properties. When the properties of the polyesters of these glycols are compared with those of the polyesters of polymethylene glycols (ethylene glycol, 1,6-hexanediol, 1,10-decanediol, and 1,20-eicosanediol) derived from the same dicarboxylic acids [1, 2, 3], it will be seen quite readily that the latter polyesters are crystalline substances, whereas the former are noncrystalline.

It should be noted also that, although in their general effects and ether linkage and a methyl side group are equivalent in the sense that they both reduce the crystallinity of the polymer, they differ greatly in effectiveness. If we base the comparison of effectiveness on the tendency to annul the evenness factor, then it may be said that the effect of a methyl group is equivalent to that of three or four ether linkages, i.e. one methyl side group is three or four times as effective as an ether linkage.

## SUMMARY

1. Some polyesters formed by diethylene glycol, triethylene glycol, and 1,2-propanediol with dicarboxylic

acids have been prepared.

2. The effect of the structures of the starting substances on the melting points and solubilities of the resulting polyesters has been discussed.

3. It has been shown that the introduction of a methyl side group into a polyester molecule produces an effect similar to that of the introduction of three or four ether linkages, the crystallinity of the polymer being greatly reduced, its melting point lowered, and its solubility raised.

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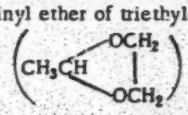
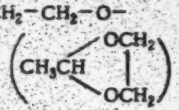
# THE OXONIUM THEORY IN THE LIGHT OF AN OPTICAL STUDY OF THE HYDROGEN BOND IN SOME MONOVINYL ETHERS OF GLYCOLS AND POLYGLYCOLS

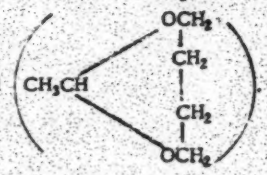
M. F. Shostakovsky, M. I. Batuev, P. V. Tyupaev, and A. D. Matveeva

One of the authors of this paper has suggested [1], in connection with the oxonium theory that he has developed on the basis of the reactions of vinyl ethers, that in these compounds the valency of oxygen is variable; according to the conditions, the oxygen behaves as a bi- or ter-valent element.

The history of investigations on oxygen-containing compounds shows that for oxygen in various compounds under various experimental conditions authors have suggested valencies not only of two and three, but also of four, and even six*. It would, of course, be of great interest to determine the nature of the observed or postulated "anomalous" valency of oxygen in these and other cases, and so determine the structures of the oxygen-containing compounds. The present investigation is a structural study of this sort applied to some vinyl ethers which have been examined with the aid of Raman spectra. At the same time we have investigated some cyclic acetals that are isomeric with these ethers.

The following monovinyl ethers of glycols and "polyglycols", and cyclic acetals isomeric with these, were synthesized and investigated optically: 1) the monovinyl ether of ethylene glycol ($CH_2=CH-O-CH_2-CH_2-OH$); 2) the monovinyl ether of 1,3-propanediol ($CH_2=CH_2-O-CH_2-CH_2-CH_2-OH$); 3) the monovinyl ether of 1,4-butanediol ($CH_2=CH-O-CH_2-CH_2-CH_2-CH_2-OH$); 4) the monovinyl ether of diethylene glycol ($CH_2=CH-O-CH_2-CH_2-O-CH_2-CH_2-OH$); 5) the monovinyl ether of triethylene glycol ($CH_2=CH-O-CH_2-CH_2-O-CH_2-CH_2-O-CH_2-CH_2-OH$);

6) the cyclic acetal of ethylene glycol  ; 7) the cyclic acetal of 1,3-propanediol 

8) the cyclic acetal of 1,4-butanediol  .

## 1. Synthesis of Minovinyl Ethers of Glycols and Polyglycols and of Cyclic Acetals of Glycols

The monovinyl ethers of ethylene glycol, 1,3-propanediol, 1,4-butanediol, diethylene glycol, and triethylene glycol were prepared by Favorsky and Shostakovsky's method [4] by the addition of 0,8-1 mole of acetylene to 1 mole of the glycol or polyglycol containing about 5% of dissolved caustic potash as catalyst. The preparations were carried out, similarly to that of the monovinyl ether of ethylene glycol described previously [5], in a rotating autoclave under a pressure of not more than 15 atm and at a temperature of 140-150°. The yields of the ethers varied from 40% to 60% on the amount of glycol that reacted. The reaction products were fractionated from a Favorsky flask. The monovinyl ether fractions taken were too wide to correspond to pure products. They were dissolved in water with the object of separating them from the somewhat lower boiling water-insoluble divinyl ethers. The solutions were separated from the divinyl ethers (sometimes by the aid of the salting-out effect of a small amount of potassium carbonate), and were then saturated with potassium carbonate. The salted-out monovinyl ethers were separated, dried carefully with potassium carbonate, and fractionated in presence of a small piece of calcined potassium carbonate in an apparatus having ground glass joints (including the thermometer). The fractions were redried before each redistillation. Products having definite constants were finally obtained.

The cyclic acetals of ethylene glycol, 1,3-propanediol, and 1,4-butanediol were prepared by the isomerization of the corresponding pure monovinyl ethers, which generally occurs almost instantaneously in presence of mineral

* For a more detailed discussion of this see our preliminary communications [2, 3].

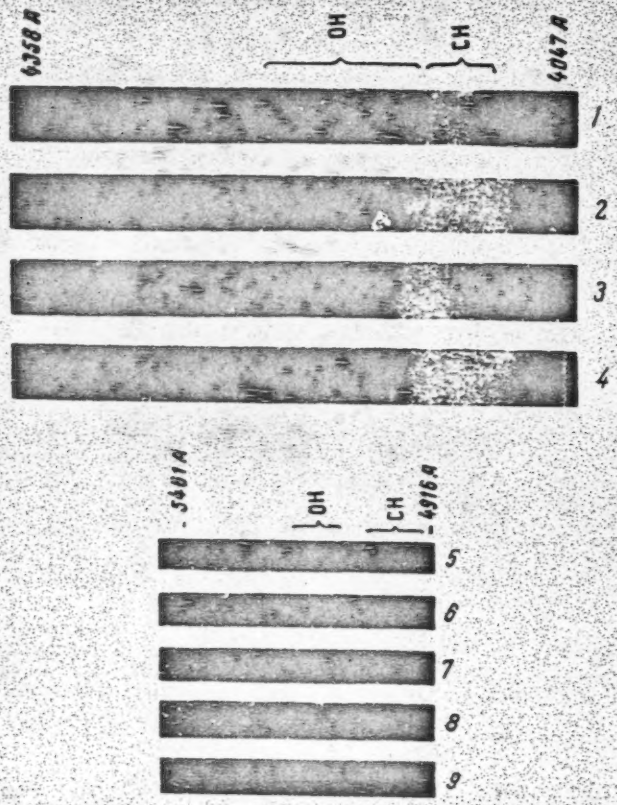



Fig. 1. Spectra of the hydroxyl groups of hydroxyl-containing compounds. Excited by the triplet 3650, 3655, 3663 A: 1) formic acid 2) methanol, 3) phenol (1, 2, and 3 are for comparison purposes); 4) monovinyl ether of ethylene glycol. Excited by the blue line 4358 A: 5) monovinyl ether of ethylene glycol; 6) monovinyl ether of 1,3-propanediol; 7) monovinyl ether of 1,4-butanediol; 8) monovinyl ether of diethylene glycol; 9) monovinyl ether of triethylene glycol.

acids, much heat being evolved. The reaction was carried out in a three-necked flask fitted with reflux condenser, mechanical stirrer, thermometer, and dropping funnel. A few drops of concentrated hydrochloric acid were placed in the flask, and the vinyl ether was then added. At first the temperature was not allowed to rise above 80°, but later the reaction mixture was brought to the boil. After cooling, it was neutralized with 1-2 ml of 10% caustic soda, dried with potassium carbonate, and distilled. The resulting acetals were treated in the cold with sodium and then distilled in absence of the sodium in an apparatus having ground glass joints (including the thermometer). The fractions were retreated with sodium before each distillation. Products having definite constants were finally obtained. The cyclic acetals of ethylene glycol and 1,3-propanediol were obtained in yields of not less than 90%, but the yield of the cyclic acetal of 1,4-butanediol was not more than 50%.

The table gives the constants of the synthesized monovinyl ethers of glycols and polyglycols and of the three cyclic acetals.

TABLE

Constants of Monovinyl Ethers of Glycols and Polyglycols and of Cyclic Acetals that are Isomeric with some of these

| Substance | B.p. (°C) (p, mm Hg) | $d_4^{20}$ | $n_D^{20}$ |
|---|---|---|---|
| Monovinyl ether of ethylene glycol | 140(745) | 0.9821 | 1.4360 |
| Monovinyl ether of 1,3-propanediol | 164(755) | 0.9611 | 1.4390 |
| Monovinyl ether of 1,4-butanediol | 182(755) | 0.9467 | 1.4458 |
| | 74.5 (7) | | |
| Monovinyl ether of diethylene glycol | 96 (12) | 1.0278 | 1.4480 |
| Monovinyl ether of triethylene glycol | 144 (14)• | 1.0525 | 1.4536 |
| Cyclic acetal of ethylene glycol | 81–2(750) | 0.9795 | 1.3972 |
| Cyclic acetal of 1,3-propanediol | 107(740) | 0.9683 | 1.4125 |
| Cyclic acetal of 1,4-butanediol | 127–128(750) | 0.9638 | 1.4280 |

## 2. Raman Spectra of the Synthesized Monovinyl Ethers of Glycols and Polyglycols and of Cyclic Acetals that are Isomeric with some of these

The Raman spectra of the synthesized monovinyl ethers and cyclic acetals were determined with a Soviet spectrograph ISP-51 having a central camera. The dispersion in the region of the line 4358 A was 26 A/mm. The spectra were excited by the mercury line 4358 A. In addition, the region of the hydroxyl group of monovinyl ethers was investigated with the mercury triplet 3650, 3655, 3663 A as exciting radiation. We give the complete Raman spectra for the substances investigated below. The intensities of the lines are given in parentheses on a visual ten-grade scale ••.

Monovinyl ether of ethylene glycol. $\Delta\nu$ ($cm^{-1}$): 246(4); 296(0); 316(2); 334(3); 356(1); 500(4b); 600(0b); 656(0); 704(3b); 810(2); 831(8); 870(0); 892(3b); 943(2); 968(2); 979(3); 1003(0); 1031(3b); 1096(3b); 1154(2); 1174(2); 1203(2); 1233(2); 1281(3); 1320(10); 1359(2d); 1393(2); 1414(2); 1459(4); 1617(7); 1638(6); 2660(0); 2722(0); 2879(6)•; 2933(10)•, 2964(2)•; 3024(6); 3044(10); 3085(0); 3120(7); ~3200–3600(3, band).

Monovinyl ether of 1,3-propanediol. $\Delta\nu$ ($cm^{-1}$): 250(3, band); 355(2b); 409(0); 497(3b); 597(2); 654(0); 686(0); 707(2); 814(5); 830(5); 870(5); 891(5), 957(3); 968(3); 1003(2); 1044(4)•; 1075(4)•; 1104(4)•; 1208(3)•; 1234(0); 1297(4), 1324(10); 1355(0); 1384(1); 1418(2); 1443(1); 1478(5); 1618(7); 1643(6); 2880(6)•; 2941(9)•; 2960(2)•; 3022(4); 3047(7); 3119(5); ~3200–3600(3, band).

Monovinyl ether of 1,4-butanediol. $\Delta\nu$ ($cm^{-1}$): 214(0); 247(6b); 303(3b); 346(0); 398(1); 450(2); 500(4); 531(1); 554(1); 588(0); 608(3); 630(0); 655(0); 679(0); 708(3); 755(1); 784(0); 823(8b); 863(3); 901(0b); 940(4)•; 971(4)•; 999(2)•; 1052(5)•; 1074(5)•; 1102(6)•; 1137(2); 1299(6); 1324(10); 1352(0); 1378(2); 1416(1); 1438(6); 1456(1); 1477(6); 1615(8); 1643(7); 2744(2)•; 2821(2)•; 2868(10b)•; 2927(10b)•; 2963(6)•; 3019(6); 3046(9); 3079(0); 3121(9); ~3200–3600(3, band).

Monovinyl ether of diethylene glycol. $\Delta\nu$ ($cm^{-1}$): 216(1); 243(4b); 289(0); 324(0); 435(0); 496(3)•; 528(2)•; 557(3)•; 611(3b); 654(0); 720(3b); 807(5)•; 849(5)•; 892(4); 962(1); 980(4); 1008(0); 1037(4)•; 1071(4)•; 1131(5b)•; 1261(3)•; 1290(3)•; 1323(10); 1455(5); 1471(5); 1620(8); 1636(6); 2877(10)•; 2942(9b)•; 3024(3); 3044(7); 3117(5); ~3200–3600(3, band).

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• In a previous paper [3] the boiling point of the monovinyl ether of triethylene glycol is also given as 144° at 1 mm.

•• The symbols appended to the intensity figures are: b - broad line, d - double line; the asterisk indicates lines having an intense background.

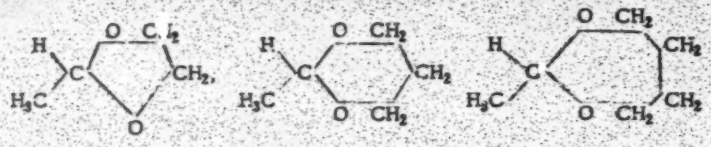
Monovinyl ether of triethylene glycol, $\Delta\nu(cm^{-1})$: 214(1); 240(45); 293(0b); 341(0b); 404(0b); 459(0b); 500(3)•; 541(2)•; 589(2)•; 623(2)•; 660(5); 807(5)•; 830(5)•; 849(5)•; 887(3); 911(0); 931(0); 973(2b); 1013(0); 1041(3)•; 1081(2)•; 1133(4)•; (5)•; 1200(1)•; 1237(2)•; 1279(3)•; 1296(3)•; 1324(0); 1400(2b); 1454(5); 1473(5); 1617(8); 1639(6); 2855(2)•; 2874(10)•; 2945(9b)•; 3022(3); 3042(6); 3083(0); 3119(4); ~3200–3600 (3, band).

Cyclic acetal of ethylene glycol, $\Delta\nu(cm^{-1})$: 175(0); 510(4b); 537(0); 693(3); 838(10); 922(0); 945(9); 1025(5b); 1091(0); 1120(6b); 1149(1); 1171(4); 1222(6b); 1282(0); 1315(3); 1356(3); 1390(0); 1413(0); 1452(6); 1481(6); 2885(6b); 2939(10); 2992(5b).

Cyclic acetal of 1,3-propanediol, $\Delta\nu(cm^{-1})$: 274(0); 349(0); 432(0); 461(6); 480(2); 501(0); 523(0); 546(0); 567(7); 589(0); 610(0); 633(0); 656(0); 680(0); 714(0); 744(0); 821(10); 855(0); 878(5); 899(0); 922(0); 935(6); 971(6); 1027(0); 1058(6); 1104(6); 1148(7); 1179(2); 1219(4); 1246(2); 1286(7); 1343(2); 1375(4)•; 1432(5); 1454(6); 1468(6); 2844(6); 2868(3); 2904(0); 2733(3); 2814(0)•; 2857(10)•; 2921(2)•; 2971(10)•; 2976(3)•; 2996(6)•.

Cyclic acetal of 1,4-butanediol, $\Delta\nu(cm^{-1})$: 207(2); 309(3); 341(4); 384(4); 428(6); 472(0); 496(0); 520(0); 542(5); 575(0); 621(1); 642(1); 779(10); 820(2); 840(2); 858(0); 922(2); 940(6); 973(6); 997(2); 1024(0); 1056(6)•; 1078(4)•; 1097(2)•; 1132(7)•; 1147(1)•; 1179(1)•; 1233(6); 1251(0); 1275(0); 1288(8); 1340(2)•; 1362(3)•; 1434(8); 1448(8); 1463(8); 2707(0); 2746(0); 2817(0)•; 2846(4)•; 2879(8)•; 2915(8)•; 2945(10)•; 2993(7)•.

There are essential differences between the spectra of the monovinyl ethers of the glycols and those of the corresponding isomeric cyclic acetals, particularly the absence in the latter of the frequencies in the neighborhood of 1600 $cm^{-1}$ (double bond region) and in the region above 3000 $cm^{-1}$ (ther frequencies of C – H at a double bond and of the hydroxyl group). We have made use of these essential differences in the optical analysis of some solutions of the investigated monovinyl ethers, as will be seen below. In passing, we may point out the lowering of the "pulsation" frequency of the ring as we proceed from a five- to a seven-membered ring in the cyclic acetals, a phenomenon observed also in the corresponding cycloalkanes:



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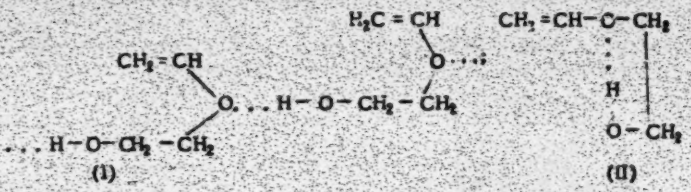
## 3. Optical Detection of the Hydrogen Bond in Monovinyl Ethers of Glycols and Polyglycols.

The above-cited spectra of monovinyl ethers of glycols and polyglycols, unlike those of the cyclic acetals investigated, contain frequencies in the region 3000-3120 $cm^{-1}$ characteristic of vibrations of C – H bonds occurring at double bonds C = C, and also frequencies in a broad diffuse band in a still higher region, this being practically the same for all of the five ethers investigated, about 3200-3600 $cm^{-1}$. This is the region of the hydroxyl frequencies.

In Fig. 1 we show this band for the spectrum of the monovinyl ether of ethylene glycol (Spectrum No. 4), the exciting radiation being the triplet 3650, 3655, 3663 A. For the other ethers investigated the band is quite similar, as will be seen from a comparison of the corresponding regions of the spectra excited by the line 4358 A (Spectra No. 5-9). For comparison, we give in Fig. 1 the spectra for the hydroxyl groups of liquid formic acid, methanol, and phenol (Spectra No. 1-3). It has been established that the presence of a broad hydroxyl band in the spectra of these substances is an indisputable criterion of the participation of the hydroxyl groups of these substances in intermolecular hydrogen bonds. An equally indisputable criterion of intermolecular hydrogen bonding is to be found in the broad diffuse band at 3200-3600 $cm^{-1}$ that we have observed in the spectra of all five of the monovinyl ethers investigated, this band being identical in general features to the hydroxyl bands of methanol, acetic acid, and phenol (we shall not consider the differences in detail in the present paper). The considerable breadth of the band and its considerable diffuseness on the low-frequency side indicates that the hydrogen bonds of monovinyl ethers of glycols and polyglycols are indeed intermolecular bonds of the type (I), and not intramolecular bonds of the type (II) [6]. If the latter are formed, then it must be at the ends of the chain (I).



(I) (II)

The intermolecular character of the hydrogen bonds of these monovinyl ethers is confirmed also by other physicochemical properties, which we shall consider below.

As is well known, the spectrum of the hydroxyl group of a molecule under conditions (in the gas phase, or dissolved in neutral solvents of the type of carbon tetrachloride, cyclohexane, benzene, etc.) which prevent hydrogen bonding is fundamentally different from that of the hydroxyl group in the liquid phase of the substance, when a hydrogen bond is formed•.

When, however, the investigated monovinyl ethers of glycols are dissolved in carbon tetrachloride, optical analysis shows that they isomerize into the corresponding cyclic acetals; no monovinyl ether molecules are present. This fact is readily established optically because of the considerable differences, noted above, between the spectra of the investigated monovinyl ethers and those of the corresponding isomeric cyclic acetals. This isomerization occurs not because the isolated molecules of the ethers are in themselves unstable and therefore undergo rearrangement into cyclic acetals, but because of the nature of the solvent, carbon tetrachloride.

The investigated monovinyl ethers are almost insoluble in cyclohexane, and two layers are formed when they are mixed. One layer is the monovinyl ether as such, and the very small portion of the monovinyl ether that passes into the cyclohexane layer does not isomerize into the cyclic acetal, as spectrum analysis shows. It is evident that in this solution vinyl ether molecules exist in the isolated state, as monomers. However, confirmation of this cannot be obtained by observations on the change in the spectrum of the hydroxyl group owing to the extremely low intensity of the hydroxyl lines resulting from the very low concentrations of the solutions, which, in their turn, are to be attributed to the very poor solubilities of the monovinyl ethers in cyclohexane.

We therefore modified the hydroxyl spectrum via a rise in temperature, determining the spectrum of a monovinyl ether of ethylene glycol at a temperature of about 85°. Owing to partial disruption of the hydrogen bonds, and also to the weakening of the hydrogen bonds that still existed, the hydroxyl band became narrower under these conditions and the intensity maximum was displaced toward the higher frequencies••. At the high-frequency limit of the band there was a readily measurable line (a triplet record was obtained from the exciting triplet 3650, 3655, 3663 A) at 3565 $cm^{-1}$. The comparatively low value of this frequency (for monomeric molecules of aliphatic monohydric alcohols, e.g. methanol, it attains a value of about 3670 $cm^{-1}$ in the gas phase) and its position at the high-frequency limit of a hydroxyl band of reduced breadth indicate that in the liquid state raising of the temperature to 85° does not result in the complete freeing of the hydroxyl groups from the influence of oxygen atoms of neighboring molecules. When, in fact, a 20% (by volume) solution of the monovinyl ether of ethylene glycol in decahydronaphthalene is heated to 85°, a line of still higher frequency is observed in the hydroxyl spectrum, namely 3625 $cm^{-1}$ (a triplet record from the exciting triplet 3650, 3655, 3663 A). Under these conditions decahydronaphthalene molecules isolate molecules of the monovinyl ether of ethylene glycol from one another, and the hydroxyl group is freed from the influence of the oxygens of other molecules of the monovinyl ether of ethylene glycol. The fact that the frequency of the hydroxyl group of the monomeric molecule of the monovinyl ether of ethylene glycol is nevertheless lower than that of the hydroxyl group of monomeric molecules of monohydric alcohols will be referred to again below.

## 4. Confirmation of the Optical Detection of a Hydrogen Bond in the Investigated Ethers by means of other Physicochemical Data

The presence of the hydrogen bond indicated by optical methods is confirmed by other physicochemical data. Thus, we have carried out molecular weight determinations on all five of the ethers investigated. It was found that with rise in concentration the degree of association increased: the monomers were converted into associated complexes, first of all dimers, and later polymers (see Fig. 2). The isomeric cyclic acetals, which would not

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• See the photograph in a paper by one of the authors [7] of the spectrum of a hydroxyl group that is not hydrogen-bonded (in the monomeric molecule of acetic acid in the gas phase), when it takes the form of a sharp line, and the spectrum of a hydroxyl group that is hydrogen-bonded (in liquid acetic acid), when it takes the form of a broad diffuse band displaced toward the lower frequencies.

•• One of the authors of this paper has established that phenol behaves similarly [8].

be expected to exhibit hydrogen bonding, were found to exist in the monomeric form, and for them the degree of association remained almost constant at unity as the concentration increased.

As a result of intermolecular hydrogen bonding, the monovinyl ethers of glycols have higher boiling points than the isomeric cyclic acetals in which no intermolecular hydrogen bonding occurs:

| | B.p. in °C (p in mm Hg) | | B.p. in °C (p in mm Hg) |
|---|---|---|---|
| Monovinyl ether of ethylene glycol | 140 (745) | Cyclic Acetal of ethylene glycol | 81–82 (750) |
| Monovinyl ether of 1,3-propanediol | 164 (755) | Cyclic Acetal of 1,3-propanediol | 107 (740) |
| Monovinyl ether of 1,4-butanediol | 182 (755) | Cyclic Acetal of 1,4-butanediol | 127–128 (750) |

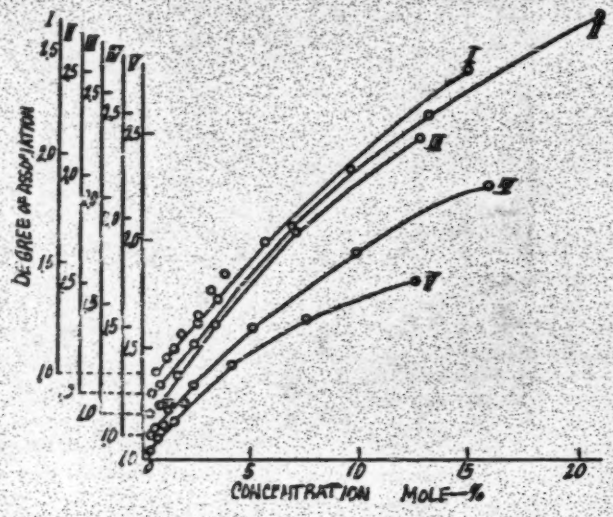


Fig. 2. Degree of association of I - monovinyl ether of ethylene glycol; II - monovinyl ether of 1,3-propanediol; III - monovinyl ether of 1,4-butanediol, IV - monovinyl ether of diethylene glycol; V - monovinyl ether of triethylene glycol; expressed as functions of the concentrations of their solutions in benzene(determined by the cryoscopic method)

The nonhydrogen-bonding cyclic acetals have also considerably lower viscosities than the corresponding ethers from which we obtained them by isomerization (viscosities in centipoise at 20°):

| | |
|---|---|
| Monovinyl ether of ethylene glycol | 2.4167 |
| Monovinyl ether of 1,3-propanediol | 4.0412 |
| Monovinyl ether of 1,4-butanediol | 5.7551 |
| Monovinyl ether of diethylene glycol | 5.2651 |
| Monovinyl ether of triethylene glycol | 9.8670 |
| Cyclic acetal of ethylene glycol | 0.6499 |
| Cyclic acetal of 1,3-propanediol | 0.8544 |
| Cyclic acetal of 1,4-butanediol | 1.0902 |

(The viscosities were determined in a Pinkevich capillary viscometer having a capillary of diameter 0.8 mm. The viscometer was calibrated with water, the viscosity of which was taken as 1.0050 centipoise at 20°. The viscometer was placed in a thermostat at 20°, and the rate of efflux was measured 30 minutes after the liquid had been introduced into the viscometer.)

Hence, the intermolecular hydrogen bonding that we detected in monovinyl ethers of glycols and polyglycols by the optical method has been unequivocally confirmed by other physicochemical data cited above. At the same time the nature of the "anomalous" valency of oxygen in the investigated ethers, which we referred to at the beginning of the paper, has been elucidated quite unequivocally: it consists in the ability of oxygen atoms in the ethers investigated to form hydrogen bonds with the hydroxyl groups of neighboring molecules as an effect

supplementary to that of the usual "normal" valencies that these oxygen atoms have at their disposal. By means of experimental optical data, which are in accord with other physicochemical data, these hydrogen bonds have been detected directly and completely unequivocally.

## 5. The Intermolecular Hydrogen Bond of the Investigated Ethers, and their Chemical Properties

The results that we have obtained are of great importance for the understanding of the behavior of various vinyl ethers, differing from one another in composition and structure.

Thus, it has been established in previous investigations by Shostakovsky and coworkers that alkyl vinyl ethers are highly reactive (readily undergoing various reactions, particularly in presence of mineral acids and metal chlorides), whereas monovinyl ethers of glycols are chemically inert. In the light of our results, this is easily understood. Thus, we regard the activation of alkyl vinyl ethers by mineral acids as the formation via a hydrogen bond of complexes that can isomerize and dissociate:

$$CH_2 = CH - O - Alk$$
$$\vdots$$
$$HCl$$

It will be clear, however, that monovinyl ethers of glycols cannot behave in this way, since their structures already contain hydrogen bonds. This is also the basis of the chemical inertness that we have established experimentally.

There can be no doubt that this inertness must be shown also by monovinyl ethers of polyglycols, though it is probable that it will not be so great, since their ether oxygens, unlike those of monovinyl ethers of glycols, cannot all take part in hydrogen bonding (in monovinyl ethers of polyglycols there are several ether oxygens per hydroxyl group).

There is a further point that is worthy of notice. We have already pointed out that in comparison with the frequency of the hydroxyl group in monohydric alcohols, the frequency of the hydroxyl is low in monovinyl ethers of glycols and polyglycols in which hydrogen bonding has been completely, or almost completely, broken down by rise in temperature to 85° in the liquid phase or by dissolution in decahydronaphthalene. This fact undoubtedly indicates that the hydrogen of the hydroxyl group of the investigated ethers in their monomeric form is more mobile than that of monohydric alcohols [7]. This view is confirmed by the following chemical data.

A study of the effect of temperature in the vinylation of monohydric alcohols (methyl, ethyl, and butyl), glycols, and polyglycols has shown that the addition of $C_2H_2$ to monohydric alcohols begins only at 150°, whereas glycols and polyglycols already react at 140°. In view of the fact that the formation of the divinyl ether proceeds stepwise (via the monovinyl ether) and that the products of the complete vinylation of glycols at 140° comprise only the divinyl ethers with insignificant amounts of the cyclic acetals (the formation of which occurs in the gas phase owing to the isomerization of the monovinyl ethers), it must be acknowledged that the hydrogens of the hydroxyls of glycols and polyglycols, and also of the hydroxyls of the monovinyl ethers of glycols and polyglycols, have practically identical mobilities, which are appreciably higher than the mobilities of the hydrogens of the hydroxyls of monohydric normal aliphatic alcohols.

## SUMMARY

An optical investigation of some monovinyl ethers of glycols and polyglycols has indicated the presence of intermolecular hydrogen bonds in the liquid state, and this is confirmed by data derived from other physicochemical investigations. The presence of an intermolecular hydrogen bond explains the "anomalous" valency of the oxygen atom of the investigated class of ethers (its "oxonium" character), and also peculiarities of the properties of these ethers.

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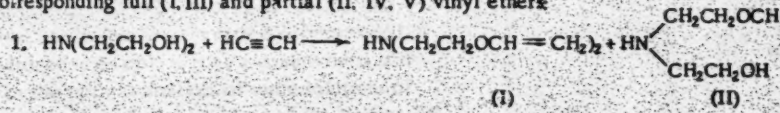
# SYNTHESIS AND REACTIONS OF VINYL ETHERS OF ETHANOLAMINES

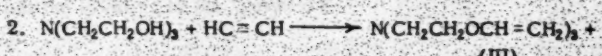
## COMMUNICATION 5. VINYL ETHERS OF DI- AND TRI-ETHANOLAMINES

M. F. Shostakovsky and I. A. Chekulaeva

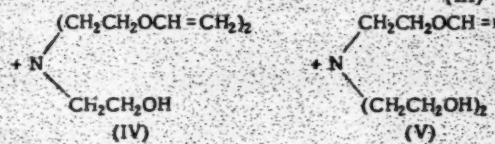
In order to determine the relationship between structure and reactivity for vinyl ethers of ethanolamines we have investigated the properties of several such substances in which the substituents present on the nitrogen were varied. In continuation of our previous investigations [1, 2, 3] we have studied the properties of vinyl ethers of di- and tri-ethanolamines. These compounds were synthesized by direct vinylation of the ethanolamines, which may yield a number of products under the conditions of the Favorsky-Shostakovsky reaction [4] owing to the presence of more than one hydroxyl group in the molecules of these substances. The vinylation of these ethanolamines did in fact yield the corresponding full (I, III) and partial (II, IV, V) vinyl ethers:



(I) (II)



(III)



(IV) (V)

In this respect di- and tri-ethanolamines are similar to ethylene glycol and glycerol [5, 6], but the vinyl ethers of di- and tri-ethanolamines did not undergo further changes resulting in the formation of cyclic products: the vinyl ethers of diethanolamine (I, III), like that of 2-aminoethanol, did not yield substances of the morpholine or oxazolidine type. Indeed, the formation of cyclic products by hydrogen transfer from a hydroxyl group is not very probable owing to steric difficulties.

In the course of the study of the vinylation of di- and tri-ethanolamines we have established also that the presence of the basic nitrogen has a considerably less effect on the vinylation reaction than in the vinylation of 2-aminoethanol and 2-diethylaminoethanol. The vinyl ethers of di- and tri-ethanolamines were formed in good yield (70-85% on the amount of the ethanolamine) in presence of caustic potash, whereas these conditions were quite unsuitable for 2-aminoethanol and 2-diethylaminoethanol, for which it was necessary to replace caustic potash by the potassium derivative of the amino alcohol [1, 2].

The structures of the vinyl ethers obtained were proved by hydrolysis and hydrogenation. The vinyl ethers of di- and tri-ethanolamines were hydrolyzed with dilute sulfuric acid, acetaldehyde and the original ethanolamine being formed. The results of the quantitative estimation of acetaldehyde showed that the mono- and di-vinyl ethers of diethanolamine (I and II) and the trivinyl ether of triethanolamine (III) were readily and completely hydrolyzed by 2% sulfuric acid at room temperature. The mono- and di-vinyl ethers of triethanolamine (IV and V) were only partially hydrolyzed under these conditions, 4-6 hours in a boiling water bath being required for their complete hydrolysis. The hydrogenation of the vinyl ethers of di- and tri-ethanolamines was carried out under pressure in presence of Raney nickel and it resulted in the formation of the corresponding ethyl ethers (Table 4).

The behavior of the vinyl ethers of di- and tri-ethanolamines toward alcohols was studied, and also their polymerization. It was found that the mono- and di-vinyl ethers of diethanolamine (I, II) were inert to the action of alcohols in presence of hydrochloric acid as catalyst (10-12 hours at 150°). Also, the monovinyl ether of diethanolamine (II) did not form an internal cyclic acetal under such conditions.

The vinyl ethers of di- and tri-ethanolamines, like those of 2-amino- and 2-diethylamino-ethanol [1, 2], did not polymerize in presence of such catalysts as concentrated hydrochloric acid and ferric chloride under the usual conditions for unsubstituted alkyl vinyl ethers. The ion-catalyzed reactions of vinyl ethers of ethanolamines and, in particular, their polymerization reactions are complicated by the presence of two centers (O and N) in these molecules that can undergo "onium" formation. It is possible that the catalyst forms stable complexes with

the vinyl ether molecule, and these have no catalytic effect for the processes concerned. We have, however, succeeded in bringing about the free-radical polymerization of vinyl ethers of di- and tri-ethanolamines by the use of 2,2'-azobis(2-methylpropionitril). The yield and properties of the resulting polymer depended on the structure of the original vinyl ether (Table 5). A peculiar feature of some of the polymers was their three-dimensional structure; their formation could result from the presence of several vinyl or other functional groups in the original monomers.

## EXPERIMENTAL

### 1. Synthesis of Vinyl Ethers of Diethanolamine (I and II)

Diethanolamine, prepared by reaction between ethylene oxide and aqueous ammonia, had the following properties: m.p. 28°; b.p. 155.5–156° and 13 mm; $n_D^{30}$ 1.4755. Its potassium derivative was prepared by reaction with potassium at 30-40°. A mixture of 65.7 g of diethanolamine, 7.3 g of its potassium derivative, and 150 ml of benzene was placed in a 2.5-liter rotating steel autoclave. The autoclave was blown out with acetylene, after which acetylene was passed in up to a pressure of 14-16 atm. The autoclave was heated to 140-150° and maintained at that temperature for 4-6 hours. It was then cooled, a fresh portion of acetylene was passed in, and the autoclave was again heated at the same temperature. The total amount of acetylene passed in was the calculated amount for the vinylation of two hydroxyl groups.

The benzene was distilled off, and the reaction products were separated by vacuum fractionation, which yielded:

| | | | |
|---|---|---|---|
| Frac. I, | b.p. 85–95° | (9 mm); | 71.7 g |
| Frac. II, | b.p. 98–110° | (9 mm); | 14.0 g |
| Frac. III, | b.p. 115–135° | (9 mm); | 1.0 g |
| Resin | | | 21.0 g |

Redistillation of Fraction I after treatment with sodium yielded 70.0 g (64.2% on the amount of diethanolamine taken) of the divinyl ether of diethanolamine (I), a colorless mobile liquid having an amine odor, soluble in ether, benzene, alcohol, acetone, and dioxane, b.p. 80.5–81.5° and 8 mm; 68–69° and 3.5 mm; $n_D^{20}$ 1.4573; $d_4^{20}$ 0.9491; found MR 45.17; calculated for $C_8H_{15}O_2N$ MR 45.09; found M (cryoscopically in benzene) 146.0; 147.4; calculated M 157.2.

| | | | | |
|---|---|---|---|---|
| | Found % | C 60.91; 61.06; | H 9.60; 9.67; | N 8.94; 9.08 |
| $C_8H_{15}O_2N$. | Calculated % | C 61.12; | H 9.61; | N 8.92 |

Repeated vacuum fractionation of Fraction II resulted in the isolation of 12.0 g (13.2% on the amount of diethanolamine taken) of the monovinyl ether of diethanolamine (II), a colorless, viscous liquid, readily soluble in ether, benzene, and alcohol, poorly soluble in water, b.p. 95° (4 mm); $n_D^{20}$ 1.4687; $d_4^{20}$ 1.007; found MR 36.24; calculated for $C_6H_{13}O_2N$ MR 36.21; found M (cryoscopically in benzene) 134.8; 136.6; calculated M 131.1.

| | | | | |
|---|---|---|---|---|
| | Found % | C 55.43; 55.24; | H 9.97; 9.95; | N 10.50; 10.69 |
| $C_6H_{13}O_2N$. | Calculated % | C 54.94; | H 9.99; | N 10.60 |

The literature [7] gives b.p. 100-110°/8 mm.

The vinylation of diethanolamine was carried out also in presence of caustic potash and in an aqueous medium. The reaction products were worked up in various ways. The results of the experiments are given in Table 1.

In the vinylation of diethanolamine, and also of triethanolamine, not only the ethanolamine, but also the acetylene, took part in the formation of resin.

### 2. Synthesis of Vinyl Ethers of Triethanolamine (III, IV, and V)

Triethanolamine was separated from the technical product by distillation and had the following constants: b.p. 178° (9.5 mm); $n_D^{21.5}$ 1.4858; $d_4^{20}$ 1.144. The preparation of vinyl ethers of triethanolamine was carried out as for diethanolamine, with the exception that caustic potash was used as catalyst. The autoclave contained 100 g of triethanolamine, 10 g of caustic potash powder, and 150 ml of benzene, and the reaction temperature was maintained in the range 150-160°. Vinylation was discontinued when about 1.8 mole of acetylene had been adsorbed per mole of triethanolamine.

After removal of solvent, the following fractions were obtained from the reaction products:

Frac. I, b.p. 65–70°, –3.5 mm; $n_D^{26}$ 1.4615; 6.5g
Frac. II, b.p. 70–115°–3.5 mm; $n_D^{20}$ 1.4645; 1.0 g
Frac. III, b.p. 115–125°– 3.5 mm; $n_D^{20}$ 1.4692; 4.5g
Frac. IV, b.p. 125–130°– 3.5 mm; $n_D^{20}$ 1.4720; 92.5g
Frac. V, b.p. 130–140°, – 3.5 mm; $n_D^{20}$ 1.4778; 15.8 g
Frac. VI, b.p. 140–145°, – 3.5 mm, $n_D^{20}$ 1.4810; 4.3g
Resin 21.3g

Redistillation of Fractions II and III after treatment with sodium yielded 4.0 g (2.6% on the triethanolamine) of the trivinyl ether of triethanolamine (III): colorless liquid having a feeble odor; soluble in ether and benzene; insoluble in water; b.p. 122° (5 mm); $n_D^{20}$ 1.4678; $d_4^{20}$ 0.9696; found MR 65.04; calculated for $C_{12}H_{21}O_3N$ MR 65.08; found M (cryoscopically in benzene 224.1; 218.9; calculated M 227.3.

Found %: C 63.39; 63.42; H 9.57; 9.54; N 6.48; 6.35
$C_{12}H_{21}O_3N$. Calculated %: C 63.40; H 9.28; N 6.16

TABLE 1

Dependence of the Yield of Vinyl Ethers of Diethanolamine on the Vinylation Conditions

| Expt. No. | Solvent | Catalyst (10% on the weight of diethanolamine) | Treatment of reaction product | Yield of crude vinyl ethers (b.p. 72-75° and 94-98° at 5 mm) (% on weight of diethanolamine taken) | Amount of resin (% on weight of diethanolamine) |
|---|---|---|---|---|---|
| 1 | Benzene | Potassium derivative | Distillation | 83–85 | 25–30 |
| 2 | Benzene | Potassium derivative | Treatment with water | 74–75 | 30–32 |
| 3 | Benzene | Caustic potash | Distillation | 70–73 | 40–45 |
| 4 | No solvent | Caustic potash | Distillation | 70–73 | 45–47 |
| 5 | Water | Caustic potash | Treatment with water | 0.0 | 116 |

Repeated fractionation of Fraction IV yielded 90.0 g (66.7% on the triethanolamine) of the divinyl ether of triethanolamine (IV): colorless liquid having a feeble odor; soluble in ether, benzene, and alcohol; insoluble in water; b.p. 125–126° (4.5 mm); $n_D^{20}$ 1.4725; $d_4^{20}$ 1.0022; found MR 56.29; calculated for $C_{10}H_{19}O_3N$ MR 56.20; found M (cryoscopically in benzene) 197.8; 195.1; calculated for $C_{10}H_{19}O_3N$ M 201.3.

Found %: C 59.59; 59.67; H 9.64; 9.60. N 7.05; 7.03
$C_{10}H_{19}O_3N$. Calculated %: C 59.66; H 9.49; N 6.95

The literature [7] gives b.p. 120–130°/8 mm.

Repeated fractionation of Fractions V and VI in a current of nitrogen yielded 4.0 g (3.4% on the triethanolamine) of the monovinyl ether of triethanolamine (V): colorless viscous liquid, which yellowed in the air; soluble in ether, benzene, and alcohol; b.p. 141–142° (3.5 mm); $n_D^{20}$ 1.4805; $d_4^{20}$ 1.0596; found MR 47.01; calculated for $C_8H_{17}O_3N$ MR 47.31; found M (cryoscopically in benzene) 180.1; 180.4; calculated M 175.2.

Found %: C 54.92; 54.84; H 9.69; 9.68; N 8.20; 8.38
$C_8H_{17}O_3N$. Calculated %: C 54.84; H 9.78; N 7.99

Fraction I yielded 6 g of a by-product, b.p. 66–67° (3.5 mm); $n_D^{20}$ 1.4613; $d_4^{20}$ 0.9702; found MR 44.50; found M 155.1; 155.9; calculated M 157.2.

Found %: C 61.33; 61.25; H 9.66; 9.52; N 9.06; 9.05
$C_8H_{15}O_2N$. Calculated %: C 61.12; H 9.62; N 8.91

The investigation of this compound with the object of determining its structure is continuing. The yield of the trivinyl ether of triethanolamine (III) can be raised to 65.0% by the use of 3 moles of acetylene per mole of

triethanolamine. Under these conditions, none of the monovinyl ether could be isolated. When one-third of this amount was absorbed, the yield of the monovinyl ether of triethanolamine (V) attained 9-10%.

The results of experiments on the vinylation of triethanolamine in presence of its potassium derivative and without solvent are given in Table 2.

TABLE 2

Dependence of the Yield of Vinyl Ethers of Triethanolamine on the Vinylation Conditions

| Expt. No. | Catalyst (10% on the weight of triethanolamine) | Solvent | Total yield of crude vinyl ethers (b.p. 115-145°/3.5 mm) (% on triethanolamine) | Amount of resin (% on triethanolamine) |
|---|---|---|---|---|
| 1 | Potassium derivative | Benzene | 80–85 | 10–15 |
| 2 | Caustic potash | Benzene | 80–85 | 20–25 |
| 3 | Caustic potash | No solvent | 80–85 | 25–30 |

The potassium derivative of triethanolamine, which was used as catalyst, was prepared by heating triethanolamine with potassium at 80-90°. In all of these experiments the amount of acetylene passed in was 3 moles per mole of triethanolamine.

It will be seen from Table 2 that the presence of benzene has no effect on the yield of vinyl ethers of triethanolamine. It is however better to carry out the vinylation in a solvent in order to dilute the acetylene (to avoid an explosion).

3. Hydrolysis of Vinyl Ethers of Di- and Tri-ethanolamines

The vinyl ethers were hydrolyzed with 2% sulfuric acid at room temperature and at higher temperatures. The acetaldehyde liberated was determined quantitatively by the bisulfite method [8]. The results of these determinations are given in Table 3.

TABLE 3

Hydrolysis of Vinyl Ethers of Ethanolamines

| Expt. No. | Ether | Degree of hydrolysis of vinyl ether (%) |
|---|---|---|
| 1 | Divinyl Ether of Diethanolamine | 95.3 |
| | | 93.5 |
| 2 | Monovinyl Ether of Diethanolamine | 100.6 |
| | | 99.6 |
| 3 | Trivinyl Ether of Triethanolamine | 97.8 |
| | | 98.9 |
| 4 | Divinyl Ether of Triethanolamine | 54.5 |
| | | 43.0 |
| | | 100.7* |
| | | 99.3* |
| 5 | Monovinyl Ether of Triethanolamine | 91.4 |
| | | 91.6 |
| | | 96.6* |
| | | 97.4* |

4. Hydrogenation of Vinyl Ethers of Di-and Tri-ethanolamines

A mixture of vinyl ether of the ethanolamine and Raney nickel (5% on the weight of the ether) was placed in a 150-ml rotating autoclave, and the calculated amount of hydrogen was passed in. For the vinylethers of diethanolamine hydrogenation took place at room temperature, but for the vinyl ethers of triethanolamine it was necessary to heat to 150°. The duration of the reaction was 10-12 hours. The reaction product was filtered from the catalyst and distilled. It was purified either by treatment with sodium in the cold followed by distillation, or merely by repeated distillation. The yield of hydrogenation products was 65-70%. The reaction was complicated by the formation of by-products, which were not investigated. The constants of the resulting ethyl ethers are given in Table 4.

5. Polymerization of Vinyl Ethers of Di- and Tri-ethanolamines in presence of 2,2'-Azobis[2-methylpropionitrile]

2,2'-Azobis[2-methylpropionitrile] was purified by recrystallization from methanol, and was obtained as colorless crystals, m.p. 105°. It was added (2% by weight) to the vinyl ether, and the mixture was heated continuously at 60-65° for 100 hours in a sealed glass tube. The treatment given to the reaction products was determined by the properties of the vinyl ethers and of their polymers. The results on the polymerization are given in Table 5.

*Results of hydrolysis at 100° for six hours.

TABLE 4

Ethyl Ethers of Di- and Tri-ethanolamines

| No. | Ether | B.p. in °C (p in mm Hg) | $n_D^{20}$ | $d_4^{20}$ | MR | | Elementary Analysis | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | found | calculated | %C | | %H | | %N | |
| | | | | | | | found | calculated | found | calculated | found | calculated |
| 1 | Diethyl ether of diethanolamine • | 84-86(14) | 1.4227 | 0.8855 | 46.32 | 46.03 | 59.74<br>59.77 | 59.60 | 11.99<br>11.83 | 11.88 | 8.79<br>8.89 | 8.69 |
| 2 | Monoethylether of diethanolamine | 90-90.5 (4.5) | 1.4471 | 0.9676 | 37.00 | 36.68 | 54.32<br>54.13 | 54.14 | 11.33<br>11.62 | 11.35 | 10.53<br>10.30 | 10.52 |
| 3 | Triethyl ether of triethanolamine•• | 104(3.5) | 1.4388 | 0.9203 | 66.65 | 66.48 | 61.82<br>61.75 | 61.77 | 11.63<br>11.64 | 11.66 | 6.07<br>5.92 | 6.00 |
| 4 | Diethyl ether of triethanolamine | 109-110 (4.5) | 1.4418 | 0.9510 | 57.14 | 57.13 | 58.95<br>58.85 | 58.50 | 11.24<br>11.41 | 11.29 | 7.18<br>7.15 | 6.82 |
| 5 | Monoethyl ether of triethanolamine | 136-137 (4.5) | 1.4635 | 1.0259 | 47.63 | 47.77 | 53.98<br>53.85 | 54.22 | 11.06<br>11.04 | 10.81 | 8.12 | 7.90 |

TABLE 5

Polymerization of Vinyl Ethers of Di- and Tri-ethanolamines in presence of 2,2'-Azobis[2-methylpropionitrile]

| Expt. No. | Ether | Yield of polymer (%) | Nitrogen content of polymer (%) | | Molecular weight | Characteristics of polymer |
|---|---|---|---|---|---|---|
| | | | found | calculated | | |
| 1 | Divinyl ether of diethanolamine | 18.4-21.1 | 8.02<br>9.09 | 8.92 | 1488<br>1550 | Thick; dark red; soluble in benzene, acetone, and alcohols |
| 2 | Monovinyl ether of diethanolamine | 5.0-7.0 | 10.70<br>10.94 | 10.67 | — | Very thick; yellow; insoluble in the usual solvents |
| 3 | Trivinyl ether of triethanolamine | 40.0-45.0 | 6.22<br>6.31 | 6.16 | — | Hard; yellow; insoluble in the usual solvents; infusible |
| 4 | Divinyl ether of triethanolamine | 19.6-19.8 | 7.10<br>6.91 | 6.95 | — | Ditto |
| 5 | Monovinyl ether of triethanolamine | 6.0 | 8.71<br>8.57 | 7.99 | — | Very thick; yellow, soluble in water and alcohols |

In Expt. No. 1 the unchanged vinyl ether was separated from the polymer by vacuum distillation, and the polyme was vacuum-dried (3 mm) at 50-60°. In Expts. No. 2-5 the polymer was precipitated from the reaction product with diet

• Data in the literature: • b.p. 198-200° [9]; •• b.p. 134-137° and 12 mm; $d_4^{23}$ 0.936 [10].

ether, washed several times with ether, and dried. Unchanged vinyl ether was separated from the ether solution by distillation. Elementary analysis and molecular weight determinations were carried out on the products isolated, and their solubilities in various solvents were examined.

## SUMMARY


1. The vinylation reactions of di- and tri-ethanolamines have been studied.

2. It has been shown that the vinylation of di- and tri-ethanolamines results in the synthesis of full and partial ethers, most of which have been prepared for the first time.

3. It has been shown that the vinyl ethers of diethanolamine, like that of 2-aminoethanol, do not undergo cyclization under the conditions of the synthesis.

4. A study has been made of some reactions of vinyl ethers of di- and tri-ethanolamines which prove their structures.

5. It has been found that the vinyl ethers of di- and tri-ethanolamines are less reactive in ion-catalyzed reactions than unsubstituted alkyl vinyl ethers.

6. It has been shown that the vinyl ethers of di- and tri-ethanolamines can polymerize in presence of 2,2'-azobis[2-methylpropionitrile].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* T.p. = C. B. translation pagination.

## BRIEF COMMUNICATIONS

# SOLUBILITY OF DOLOMITE IN WATER IN PRESENCE OF CARBONIC ACID

O. K. Yanatyeva

The contradictory views expressed in the literature concerning the solubility relations of dolomite ($CaCO_3 \cdot MgCO_3$) arise from the absence of experimental data on its solubility. In order to resolve this controversial question, we have made a systematic investigation of the properties of dolomite and have made a very full survey of the dependence of its solubility on conditions, particularly on the partial pressure of carbon dioxide.

The solubility of dolomite and of its mixtures with calcite and magnesite was determined for various temperatures (0°, 55°, 70°) at a given partial pressure of $CO_2$ (about 1 atm), and for different partial pressures of $pCO_2$ (about 1 atm, and 0.0012 atm) at a given temperature (25°). The starting materials and the experimental procedure were essentially the same as those previously described [1, 2]. An exception was the Shishim dolomite used: this was purer, no magnesite impurity being present; its composition was 0.27% of insoluble residue, 0.40% of sesquioxides, 53.74% of $CaCO_3$, and 45.46% of $MgCO_3$.

In the work at a low partial pressure of $CO_2$ ($pCO_2$), laboratory air was used, this being blown through the reaction vessels with the aid of a water pump. The results of the investigation are given in Fig. 1 in the form of polytherm-polybars of the ternary system $CaCO_3-MgCO_3-H_2O$. All the isotherms of the system consist of three branches, corresponding respectively to the crystallization of calcite, dolomite, and magnesite; but the isotherms vary in character.

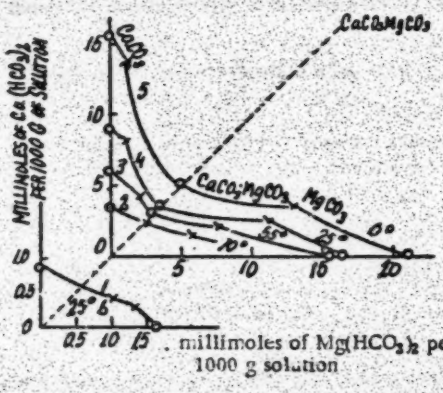


Fig. 1. Polytherm-polybar of the system $CaCO_3-MgCO_3-H_2O$. 1- about 0.0012 atm; 2, 3, 4, 5 - ~1 atm ($pCO_2$)

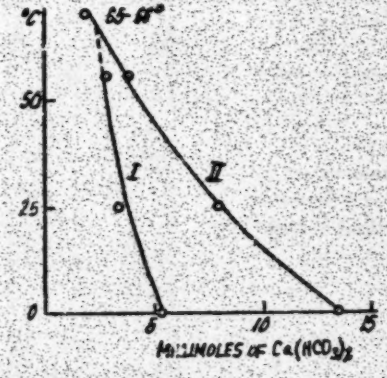


Fig. 2. Solubility polytherms of dolomite and its mixtures with calcite: I - dolomite; II - dolomite + calcite

The broken line joining the point representing the composition of dolomite with the origin (the bisector of the angle made by the axes) intersects the dolomite crystallization isotherms 3, 4, and 5 in points corresponding to the solubility of pure dolomite, thus indicating that dolomite dissolves congruently (without decomposition into its components). The point for cocrystallization of dolomite and calcite (the point a on isotherm 5, Fig. 1) is gradually displaced from the ordinate axis toward the bisector as the temperature rises, and at 70° it has already passed over to the right of the bisector. In other words, at 70° the bisector no longer intersects the dolomite branch of the isotherm; it intersects the calcite branch, which indicates that dolomite now has incongruent solubility (dissolves with decomposition). It will be clear that the temperature at which the point a falls on the bisector must be the temperature of the transition from congruent to incongruent solubility of dolomite.

The polythermal solubility curves for pure dolomite and its mixtures with calcite at a $pCO_2$ of about 1 atm intersect at a point corresponding to a temperature of 65-66° (Fig. 2), and this will be the transition temperature for

these conditions. As is well known, the solubility of $CO_2$ in water falls as the temperature rises [3]. As the $CO_2$ content of the solution falls (in spite of the fact that $pCO_2$ above the solution remains at about 1 atm), there are corresponding falls in the solubilities of calcite, magnesite, and dolomite (Table and Fig. 1), and there is a simultaneous change in the character of the solubility of dolomite.

TABLE

Solubilities of Dolomite, Calcite, and Magnesite

| Temperature (°C) | $pCO_2$ (atm) | Dolomite | Calcite | Magnesite |
|---|---|---|---|---|
| | | (millimoles of $(HCO_3)_2$ in 1000 g of solution | | |
| 0 | 1 | 10.74 | 15.08 | 22.52 |
| 25 | 1 | 6.49 | 9.0 | 16.50 |
| 55 | 1 | 6.08 | 6.09 | 15.59 |
| 70 | 1 | 4.58 | 3.45 | — |
| 25 | 0.0012 | 1.42 | 0.81 | 1.65 |

When we studied the system at 25° under a $pCO_2$ of 0.0012 atm, we obtained unequivocal confirmation of the existence of incongruent solubility of dolomite at low concentrations of $CO_2$ in the solution (isotherm 1, Fig. 1). It will be seen from the diagrams that the crystallization field of dolomite is gradually being narrowed. In the solutions of this system, therefore, dolomite is stable only at certain temperatures and at certain values of $pCO_2$. It must be pointed out also that the solubilities of the carbonates investigated vary in different ways with changes in the conditions. A comparative examination of the data in the table shows that magnesite is always the most soluble. At a $pCO_2$ of about 1 atm, dolomite is the least soluble, whereas at a $pCO_2$ of about 0.0012 atm, calcite is the least soluble, dolomite then taking up second position in the three carbonates. Hence, when the solubility of dolomite is incongruent, its value is higher in comparison with the solubility of calcite than when its solubility is congruent. For a value of $pCO_2$ of about 0.0012 atm and a temperature of 25°, the composition of an equilibrium solution obtained from an initial mixture of dolomite + water always lies at the point on the diagram corresponding to the cocrystallization of dolomite and calcite (the point b on isotherm 1 in Fig. 1), i.e. the values of the solubilities of pure dolomite and of its mixtures with calcite fully coincide at low values of $pCO_2$, the composition being 0.40 millimole of Ca, 1.02 of Mg, and 1.42 of $(HCO_3)_2$ per 1000 g of solution.

This fact is of significance for the use of carbonate rocks for under-water construction, since dolomites, dolomitic limestones, calcareous dolomites, and other such rocks should have practically the same solubilities at low partial pressures of $CO_2$, such as are found under natural conditions. The results of the investigation are also of significance for the determination of the conditions under which primary and secondary dolomites have been formed. It follows from the solubility diagram (Fig. 1) that these conditions include low temperatures and values of $pCO_2$ that are high, though different for each particular case.

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# SYNTHESIS AND REACTIONS OF OXYGEN-CONTAINING ORGANOSILICON COMPOUNDS

## COMMUNICATION 1. SYNTHESIS AND SOME PROPERTIES OF TRIALKYL- AND DIALKYLARYL-(2-CHLOROETHOXY)SILANES

M. F. Shostakovsky, D. A. Kochkin, and V. M. Vlasov

In previous papers we have laready described the preparation of some new oxygen-containing organosilicon compounds, namely organosilicon acetals prepared by the reaction of trialkyl(and aryl)silanols with vinyl ethers [1, 2, 3]. The trialkyl- and dialkylaryl-(2-haloethoxy)silanes described below, which have the general structure $XCH_2CH_2 \cdot OSiR_3$ (X is halogen; R is alkyl or aryl), form a further example of oxygen-containing organosilicon compounds, and they are of great theoretical interest.

There are several possible methods for the preparation of such compounds. It was found that they were most conveniently prepared by the action of ethylene oxide on alkyl(or alkylaryl)chlorosilanes, and in the present paper we shall describe the syntheses by this method of (2-chloroethoxy)-trimethyl-, -ethyldimethyl-, -diethylmethyl-, -triethyl-, and -diethylphenyl-silanes.

There is little information in the literature on the preparation and properties of compounds of this type. There are only a few results relating to the reactions of ethylene oxide with silicon tetrachloride, chloromethylsilane, and chloroethylsilane [4, 5]. The syntheses of (2-chloroethoxy)-ethyldimethyl-, -diethylmethyl-, and -diethylphenyl-silanes have not been described in the literature. The reaction of trialkyl(or aryl)chlorosilanes with ethylene oxide may be represented as follows:

$$R_3SiCl + CH_2-CH_2 \longrightarrow R_3SiOCH_2CH_2Cl \quad (R = CH_3-,\ C_2H_5-,\ C_6H_5-\ \text{etc.})$$
$$\qquad\qquad\quad \diagdown\ \diagup \quad\quad\quad\

TABLE 1

Physicochemical Properties of some Trialkyl- and Dialkylaryl—(2-chloroethoxy)silanes

| Name of substance | Formula | Original organosilicon compound | | | |
|---|---|---|---|---|---|
| | | Formula | $n_D^{20}$ | $d_4^{20}$ | b.p. in °C (p in mm Hg) |
| (2-Chloroethoxy)trimethylsilane | $(CH_3)_3SiOCH_2CH_2Cl$ | $(CH_3)_3SiCl$ | 1.3804 | 0.8580 | 58.0 (757) mm |
| (2-Chloroethoxy)ethyldimethylsilane | $(CH_3)_2(C_2H_5)SiOCH_2CH_2Cl$ | $(CH_3)_2(C_2H_5)SiCl$ | 1.4105 | 0.8657 | 89.0 |
| (2-Chloroethoxy)diethylmethylsilane | $(CH_3)(C_2H_5)_2SiOCH_2CH_2Cl$ | $(CH_3)(C_2H_5)_2SiCl$ | 1.4259 | 0.8936 | 119.0 |
| (2-Chloroethoxy)triethylsilane | $(C_2H_5)_3SiOCH_2CH_2Cl$ | $(C_2H_5)_3SiCl$ | 1.4320 | 0.8977 | 143-145 (757) |
| (2-Chloroethoxy)diethylphenylsilane | $(C_2H_5)_2(C_6H_5)SiOCH_2CH_2Cl$ | $(C_2H_5)_2(C_6H_5)SiCl$ | 1.5130 | 1.0252 | 227-230 (757) |

30° The ethereal solution was distilled, and a further distillation of the reaction product then yielded 16.00 g (82.0%) of (2-chloroethoxy)triethylsilane, b.p. 70.0-70.3 (5.5 mm); $n_D^{20}$ 1.4406; $d_4^{20}$ 0.9499. Found $MR_D$ 54.40; calculated for $C_8H_{19}SiOCl$ $MR_D$ 54.12.

Found %: C 49.48; 49.51; H 9.75; 9.62; Cl 18.00; 18.10
$C_8H_{19}SiOCl$. Calculated %: C 49.33; H 9.83; Cl 18.28

2. Hydrolysis of (2-Chloroethoxy)triethylsilane

The hydrolysis was carried out in a three-necked flask provided with stirrer, dropping funnel, and thermometer. A mixture of 19.5 g (0.1 mole) of (2-chloroethoxy)triethylsilane, 100 ml of ether, and 1-2 drops of phenolphthalein indicator was prepared in the flask, and this was then stirred while 200-210 ml of 2% NaOH was added slowly over a period of one hour. Stirring was continued for 3-4 hours. Fractionation of the ether layer yielded 9.5 g (72.8%) of triethylsilanol, b.p. 154° (757 mm); $n_D^{20}$ 1.4240; $d_4^{20}$ 0.8645.

## SUMMARY

1. The reaction of ethylene oxide with the following trialkyl(or aryl)chlorosilanes has been investigated: chlorotrimethyl-, chloroethyldimethyl-, chlorodiethylmethyl-, chlorotriethyl-, and chlorodiethylphenyl-silanes.

2. The following compounds have been prepared for the first time and characterized: (2-chloroethoxy)-triethyl-, and (2-chloroethoxy)diethylphenyl-silanes.

3. The proposed method is probably general for the preparation of various trialkyl(or aryl) (2-haloethoxy) silanes from ethylene oxide and trialkyl(or aryl)chlorosilanes.

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| Yield of 2-chloroethoxy derivative (%) | B.p. in °C (p in mm Hg) | $n_D^{20}$ | $d_4^{20}$ | $MR_D$ | | Analysis (%) | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | C | | H | | Cl | |
| | | | | Found | Calculated | Found | Calculated | Found | Calculated | Found | Calculated |
| 86.44 | 130-131 (758) | 1.4142 | 0.9460 | 40.51 | 40.35 | 39.29 | 39.31<br>39.20 | 8.58 | 8.88<br>8.60 | 23.24 | 23.00<br>23.15 |
| 84.6 | 71-72 (39) | 1.4262 | 0.9467 | 45.14 | 44.97 | 45.14 | 45.29<br>45.20 | 9.07 | 9.10<br>9.00 | 21.26 | 21.00<br>21.20 |
| 90.2 | 67-68 (13) | 1.4316 | 0.9478 | 49.77 | 49.41 | 46.52 | 46.67<br>46.70 | 9.48 | 9.32<br>9.54 | 19.62 | 19.12<br>19.41 |
| 82.0 | 70.0-70.3 | 1.4406 | 0.9499 | 54.45 | 54.12 | 49.33 | 49.48<br>49.51 | 9.83 | 9.75<br>9.62 | 18.28 | 18.00<br>18.10 |
| 80.1 | 128-130 (7.0)<br>(5.5) | 1.5062 | 1.0562 | 69.59 | 69.09 | 59.35 | 59.09<br>59.00 | 7.82 | 7.66<br>7.45 | 14.60 | 14.35<br>14.30 |

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# SYNTHESIS OF DIALLYLSILANES

A. D. Petrov, V. F. Mironov, and V. G. Glukhovtsev

Only four diallylsilanes ($CH_2 = CHCH_2)_2SiR_2$ are known: $(C_2H_5)_2Si(C_3H_5)_2$ [1], $CH_3HSi(C_3H_5)_2$ [2], $(CH_3)_2Si(C_3H_5)_2$ [2], and $H_2Si(C_3H_5)_2$ [3]. Diallylsilanes, however, are beginning to be used in copolymerization reactions, which may be carried out under atmospheric pressure [4], or under high pressures. With the object of extending our knowledge of the properties of diallylsilanes, in the present investigation we have synthesized four new diallylsilanes, including three containing aryl radicals (see table). The properties of the previously unknown dichloromethyl-1-naphthylsilane are also given in the table. Apart from the synthesis of the new diallylsilanes, we had occasion to repeat the syntheses of some mono-, di-, and tri-allylsilanes, and for this purpose we used allyl chloride, bromide, and iodide. As stated in a previous communication [2], the replacement of allyl chloride by the bromide greatly reduces (by a factor of 5-8) the amount of ether needed. Allyl iodide [5] requires the same reaction conditions as the bromide (except that it is necessary to distil over sodium to remove the iodine liberated), and it gives higher yields of $(CH_3)_3SiC_3H_5$, $(CH_3)_2Si(C_3H_5)_2$, and $(C_2H_5)_3SiC_3H_5$ than allyl bromide. It was found, however, that allyl iodide cannot be used at all for the synthesis of $(C_6H_5)_2Si(C_3H_5)_2$, $(1\text{-}C_{10}H_7)CH_3Si(C_3H_5)_2$, and $C_6H_5CH_3Si(C_3H_5)_2$, and low yields are obtained of $CH_3Si(C_3H_5)_3$ and $C_2H_5HSi(C_3H_5)_2$, since these substances undergo much polymerization during rectification.

TABLE

Diallylsilanes and Alkylaryldichlorosilanes

| No. | Diallylsilane | B.p. in °C (p in mm Hg) | $n_D^{20}$ | $d_4^{20}$ | MRD** | | Yield (%) |
|---|---|---|---|---|---|---|---|
| | | | | | found | calculated | |
| 1 | $(C_2H_5)HSi(C_3H_5)_2$* | 147.5 (740) | 1.4510 | 0.7808 | 48.37 | 48.36 | 29 |
| 2 | $(CH_3)_2Si(C_3H_5)_2$ | 135.5 (760) | 1.4420 | 0.7679 | 48.20 | 48.22 | 77.5 |
| 3 | $(C_6H_5)_2Si(C_3H_5)_2$* | 140.5 (2) | 1.5750 | 0.9955 | 87.77 | 87.86 | 62 |
| 4 | $(C_6H_5)CH_3Si(C_3H_5)_2$* | 242 (770) | 1.5220 | 0.9095 | 67.85 | 68.04 | 73.2 |
| 5 | $(1\text{-}C_{10}H_7)CH_3Si(C_3H_5)_2$* | 140 (1) | 1.5879 | 0.9908 | 85.72 | 83.34 | 53.2 |
| 6 | $C_6H_5(CH_3)SiCl_2$ | 206-7(757) | 1.5180 | 1.1866 | 48.80 | 49.32 | 56 |
| 7 | $1\text{-}C_{10}H_7(CH_3)SiCl_2$* | 122 (1) | 1.6025 | 1.2333 | 66.98 | 64.66 | 33.2 |

Diallylethylsilane $C_2H_5HSi(C_3H_5)_2$ (1). A mixture of 25.3 g of $C_2H_5HSiCl_2$ and 100 g of $C_3H_5I$ was added over a period of four hours to 20 g of Mg contained in 250 ml of ether. The ether was distilled off, and the residue was heated for two hours in a boiling water bath. The yield of (1) was 8 g, the remainder being high-boiling polymer.

| | | | |
|---|---|---|---|
| | Found %: | C 68.26; 68.40; | H 11.24; 11.46 |
| $C_8H_{16}Si$ | Calculated %: | C 68.5; | H 11.5 |

Diallyldimethylsilane $(CH_3)_2Si(C_3H_5)_2$ (2). A mixture of 129 g of $(CH_3)_2SiCl_2$ and 504 of $C_3H_5I$ was added over a period of ten hours to 110 g of Mg in 1 liter of ether. The ether was removed, and the residue heated for ten hours at about 100°. The yield of (2) was 112 g.

Diallyldiphenylsilane $(C_6H_5)_2Si(C_3H_5)_2$ (3). A mixture of 38 g of $(C_6H_5)_2SiCl_2$ and 35 g of $C_3H_5Cl$ was added over a period of 2 hours 30 minutes to 22 g of Mg in 800 ml of ether. The residue after removal of ether was heated for about eight hours in a boiling water bath. The yield of (3) was 28 g.

| | | | | |
|---|---|---|---|---|
| | Found %: | C 82.15; 82.30; | H 7.74; 7.77; | Si 10.26; 10.57 |
| $C_{18}H_{20}Si$. | Calculated %: | C 81.76; | H 7.62; | Si 10.61 |

Diallylmethylphenylsilane $CH_3C_6H_5Si(C_3H_5)_2$ (4). A mixture of 120 g of $(CH_3)C_6H_5SiCl_2$ and 135 g of $C_3H_5Cl$ was added over a period of four hours to 66 g of Mg in 3 liters of ether. The ether was driven off, and the residue

* Prepared for the first time.

** In the calculation, the corrections that we have introduced for the allyl group [6] and the ethyl group [3] are taken into account.

was heated for ten hours at about 100°. The yield of (4) was 93 g.

| | | |
|---|---|---|
| | Found %: | C 77.27; 77.11; H 8.82; 8.94; Si 13.90; 14.08 |
| $C_{13}H_{18}Si$. | Calculated %: | C 77.17; H 8.97; Si 13.87 |

Diallylmethyl-1-naphthylsilane 1-$C_{10}H_7CH_3Si(C_3H_5)_2$ (5). A mixture of 75 g of 1-$C_{10}H_7CH_3SiCl_2$ and 98 g of $C_3H_5Cl$ was added over a period of 90 minutes to 47 g of Mg in 1800 ml of ether. After removal of ether, the residue was heated for twelve hours. The yield of (5) was 39 g.

| | | |
|---|---|---|
| | Found %: | C 80.83; 80.84; H 8.02; 8.11; Si 11.25; 11.04 $C_{17}H_{20}Si$. |
| $C_{17}H_{20}Si$. | Calculated %: | C 80.90; H 7.99; Si 11.12 |

Dichloromethyl-1-naphthylsilane 1-$C_{10}H_7CH_3SiCl_2$ (7). 1-Naphthyllithium, prepared in 1 liter of ether from 28.9 g of Li and 414 g of 1-$C_{10}H_7Br$ was added to an ice-cooled solution of 480 g of $CH_3SiCl_3$ in 500 ml of ether; the addition was spread over 35 minutes. After four hours the precipitate was filtered off. Two distillations yielded 160 g of (7).

| | | |
|---|---|---|
| | Found %: | C 55.01; 54.96; H 4.21; 4.22; Cl 29.10; 29.70; Si 11.93; 11.78 |
| $C_{11}H_{10}SiCl_2$. | Calculated %: | C 54.78; H 4.48; Cl 29.40; Si 11.64 |

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